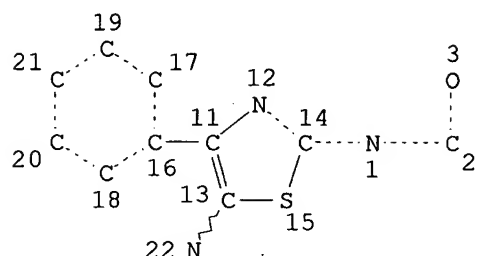


=> d 18  
 L8 HAS NO ANSWERS  
 L8 STR



NODE ATTRIBUTES:  
 DEFAULT MLEVEL IS ATOM  
 DEFAULT ECLEVEL IS LIMITED

GRAPH ATTRIBUTES:  
 RING(S) ARE ISOLATED OR EMBEDDED  
 NUMBER OF NODES IS 15

STEREO ATTRIBUTES: NONE

=> d his

(FILE 'HOME' ENTERED AT 08:55:09 ON 03 APR 2007)

FILE 'CAPLUS' ENTERED AT 08:55:18 ON 03 APR 2007

L1 1 S US2003195231/PN  
 L2 ANALYZE L1 1 RN : 245 TERMS

FILE 'REGISTRY' ENTERED AT 08:55:42 ON 03 APR 2007

L3 245 S L2  
 L4 218 S L3 AND THIAZO?  
 L5 0 S L4 AND PIPERIDIN?  
 L6 0 S L4 AND PIPERAZI?  
 L7 1 S L4 AND MORPHOL?  
 L8 STRUC  
 L9 0 SEARCH L8 SSS SUB=L3 FUL  
 L10 6 S L8  
 L11 1 S C18 H15 N3 O2 S/MF AND L10

FILE 'CAPLUS' ENTERED AT 08:59:09 ON 03 APR 2007

L12 0 S L11

FILE 'CHEMCATS' ENTERED AT 08:59:35 ON 03 APR 2007

L13 1 S L11

FILE 'REGISTRY' ENTERED AT 09:00:09 ON 03 APR 2007

L14 106 S L8 FUL

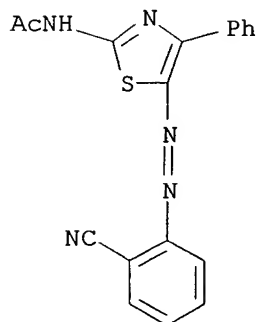
FILE 'CAPLUS' ENTERED AT 09:00:30 ON 03 APR 2007

L15 26 S L14  
 L16 15 S L15 AND PY<2002

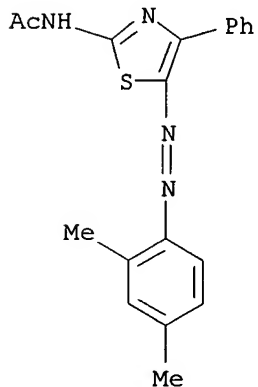
FILE 'REGISTRY' ENTERED AT 09:02:39 ON 03 APR 2007

=> d bib abs hitstr 1-15

L16 ANSWER 1 OF 15 CAPLUS COPYRIGHT 2007 ACS on STN  
AN 2001:506890 CAPLUS  
DN 136:136226  
TI Novel synthesis of thiazole disperse dye derivatives  
AU Elkholy, Yehya Mahmoud; Erian, Ayman wahba; Helal, Maher Helmy  
CS Chemistry Department, Faculty of Science, Helwan University, Cairo, Egypt  
SO Pigment & Resin Technology (2001), 30(3), 168-170  
CODEN: PGRTBC; ISSN: 0369-9420  
PB MCB University Press  
DT Journal  
LA English  
OS CASREACT 136:136226  
AB The synthesis and testing of a group of dyes derived from  
2-amino-4-phenylthiazole coupling component and aromatic amine diazo  
components is described. A comparative anal. of the dyes' washing,  
perspiration, and rubbing fastness when applied to nylon 6 and polyester  
fabrics is given.  
IT 391900-75-7P 391900-76-8P  
RL: SPN (Synthetic preparation); TEM (Technical or engineered material  
use); PREP (Preparation); USES (Uses)  
(dye; preparation of thiazole disperse azo dyes)  
RN 391900-75-7 CAPLUS  
CN Acetamide, N-[5-[(2-cyanophenyl)azo]-4-phenyl-2-thiazolyl]- (9CI) (CA  
INDEX NAME)

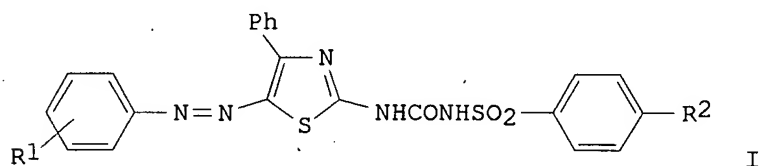


RN 391900-76-8 CAPLUS  
CN Acetamide, N-[5-[(2,4-dimethylphenyl)azo]-4-phenyl-2-thiazolyl]- (9CI)  
(CA INDEX NAME)

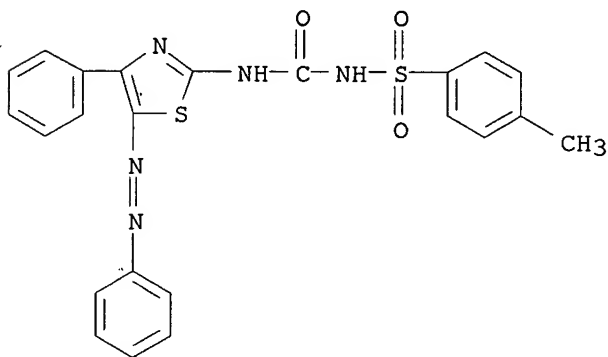


RE.CNT 11 . THERE ARE 11 CITED REFERENCES AVAILABLE FOR THIS RECORD  
ALL CITATIONS AVAILABLE IN THE RE FORMAT

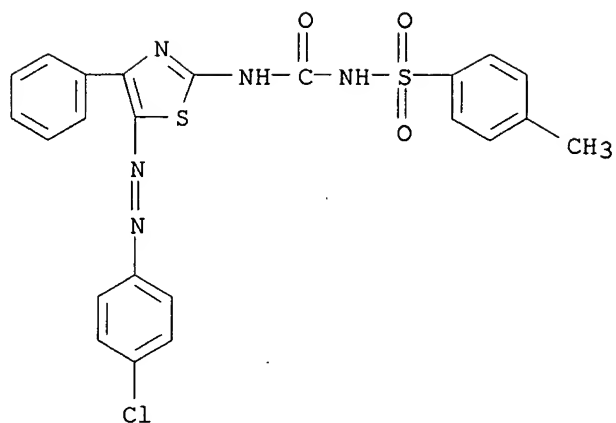
L16 ANSWER 2 OF 15 CAPLUS COPYRIGHT 2007 ACS on STN  
AN 1987:149243 CAPLUS  
DN 106:149243  
TI Synthesis of some new N1-[5-arylazo-4-phenyl-2-thiazolyl]-N-arylsulfonyl  
ureas as oral hypoglycemic agents  
AU Husain, M. I.; Jamali, M. Raghib; Srivastava, R. C.  
CS Dep. Chem., Lucknow Univ., Lucknow, 226 007, India  
SO Indian Drugs (1986), 24(1), 21-3  
CODEN: INDRBA; ISSN: 0019-462X  
DT Journal  
LA English  
GI



AB N1-[5-Arylazo-4-phenyl-2-thiazolyl]-N3-arylsulfonylureas (I, R1 = H, 2-NO2, 2-OMe, or 4-Cl and R2 = H, Me, OMe, NHAc) were prepared by the reaction of Et N-arylsulfonylcarbamates with 2-amino-4-phenyl-5-arylazothiazoles in toluene. I decreased blood sugar in rats up to 21% at an oral dose of 250 mg/kg.  
IT 107603-61-2P 107603-62-3P 107603-63-4P  
107603-64-5P 107603-65-6P 107603-66-7P  
107603-67-8P 107603-68-9P 107603-69-0P  
107603-70-3P 107603-71-4P 107605-27-6P  
107605-28-7P 107605-29-8P 107633-71-6P  
107633-94-3P  
RL: SPN (Synthetic preparation); PREP (Preparation)  
(preparation and oral hypoglycemic activity of)  
RN 107603-61-2 CAPLUS  
CN Benzenesulfonamide, 4-methyl-N-[[[4-phenyl-5-(phenylazo)-2-thiazolyl]amino]carbonyl]- (9CI) (CA INDEX NAME)

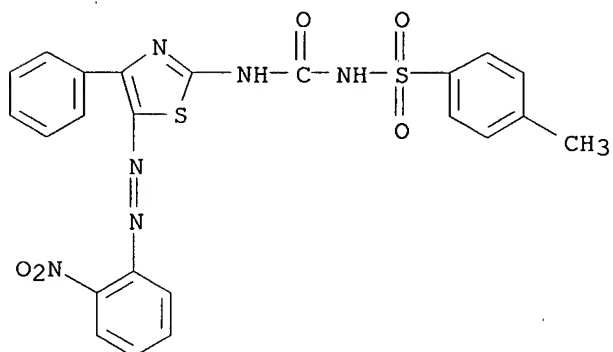


RN 107603-62-3 CAPLUS  
CN Benzenesulfonamide, N-[[[5-[(4-chlorophenyl)azo]-4-phenyl-2-thiazolyl]amino]carbonyl]-4-methyl- (9CI) (CA INDEX NAME)



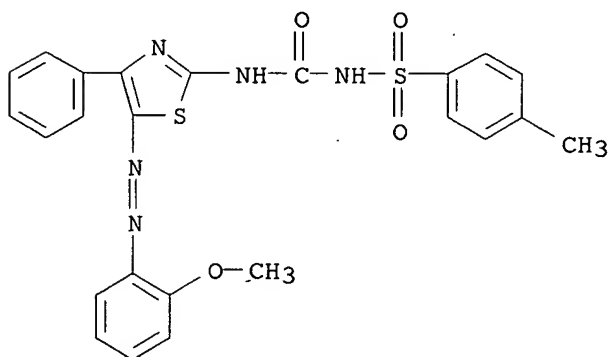
RN 107603-63-4 CAPLUS

CN Benzenesulfonamide, 4-methyl-N-[[[5-[(2-nitrophenyl)azo]-4-phenyl]-2-thiazolyl]amino]carbonyl]- (9CI) (CA INDEX NAME)



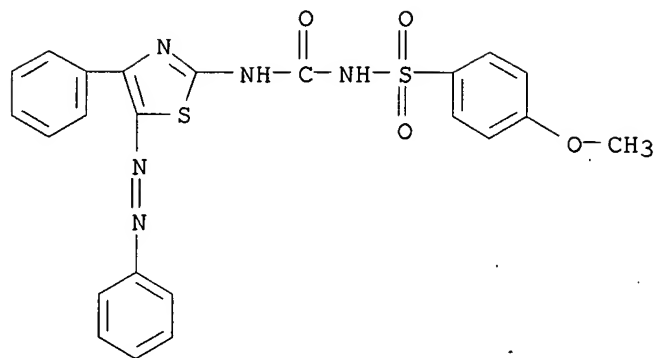
RN 107603-64-5 CAPLUS

CN Benzenesulfonamide, N-[[[5-[(2-methoxyphenyl)azo]-4-phenyl]-2-thiazolyl]amino]carbonyl]-4-methyl- (9CI) (CA INDEX NAME)



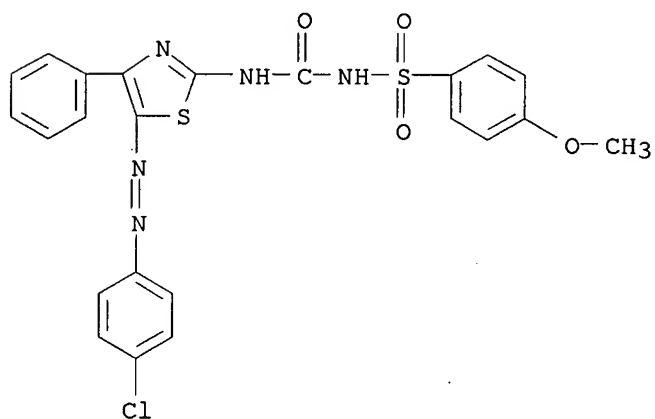
RN 107603-65-6 CAPLUS

CN Benzenesulfonamide, 4-methoxy-N-[[[4-phenyl-5-(phenylazo)-2-thiazolyl]amino]carbonyl]- (9CI) (CA INDEX NAME)



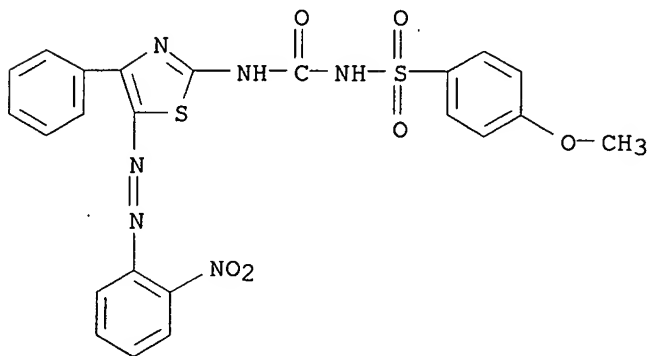
RN 107603-66-7 CAPLUS

CN Benzenesulfonamide, N-[[[5-[(4-chlorophenyl)azo]-4-phenyl-2-thiazolyl]amino]carbonyl]-4-methoxy- (9CI) (CA INDEX NAME)



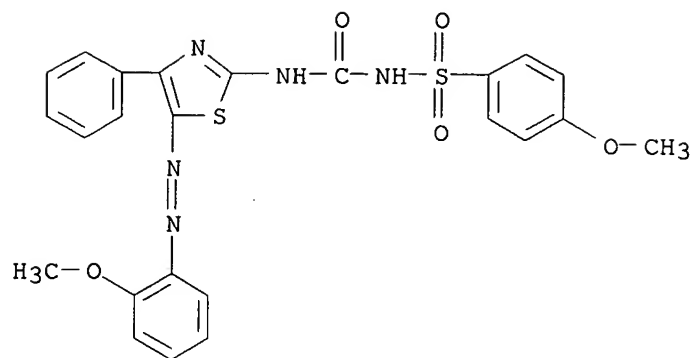
RN 107603-67-8 CAPLUS

CN Benzenesulfonamide, 4-methoxy-N-[[[5-[(2-nitrophenyl)azo]-4-phenyl-2-thiazolyl]amino]carbonyl]- (9CI) (CA INDEX NAME)



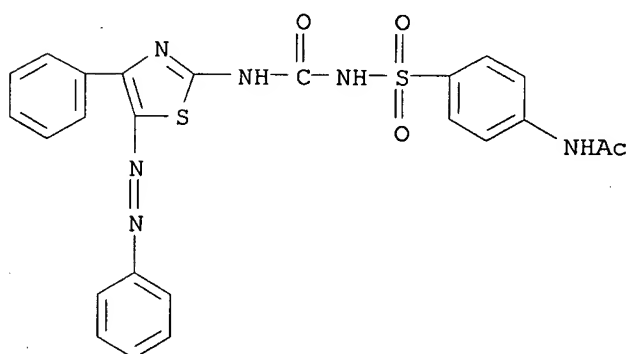
RN 107603-68-9 CAPLUS

CN Benzenesulfonamide, 4-methoxy-N-[[[5-[(2-methoxyphenyl)azo]-4-phenyl-2-thiazolyl]amino]carbonyl]- (9CI) (CA INDEX NAME)



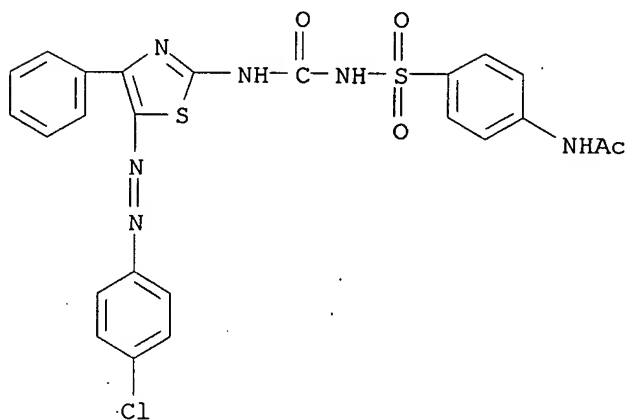
RN 107603-69-0 CAPLUS

CN Acetamide, N-[4-[[[4-phenyl-5-(phenylazo)-2-thiazolyl]amino]carbonyl]amino]sulfonyl]phenyl]- (9CI) (CA INDEX NAME)



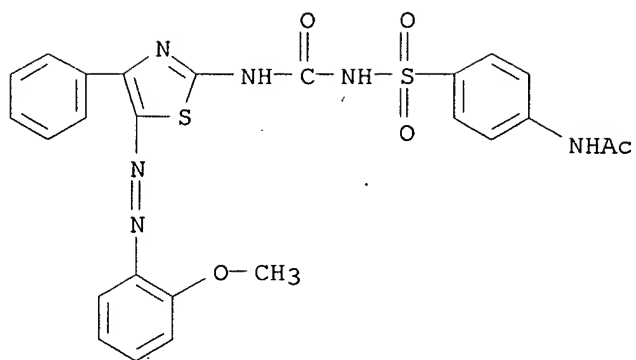
RN 107603-70-3 CAPLUS

CN Acetamide, N-[4-[[[5-[(4-chlorophenyl)azo]-4-phenyl-2-thiazolyl]amino]carbonyl]amino]sulfonyl]phenyl]- (9CI) (CA INDEX NAME)



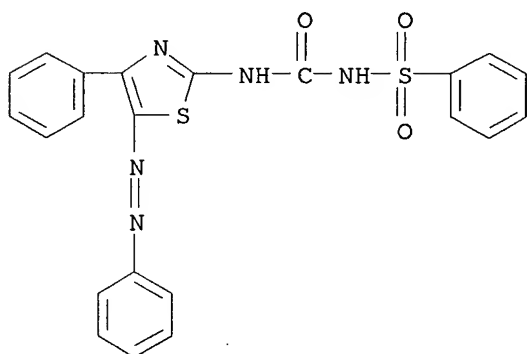
RN 107603-71-4 CAPLUS

CN Acetamide, N-[4-[[[5-[(2-methoxyphenyl)azo]-4-phenyl-2-thiazolyl]amino]carbonyl]amino]sulfonyl]phenyl]- (9CI) (CA INDEX NAME)



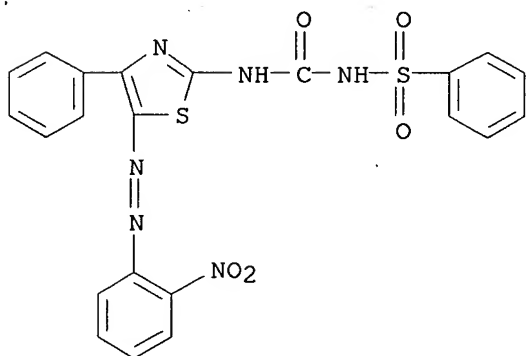
RN 107605-27-6 CAPLUS

CN Benzenesulfonamide, N-[[[4-phenyl-5-(phenylazo)-2-thiazolyl]amino]carbonyl]- (9CI) (CA INDEX NAME)



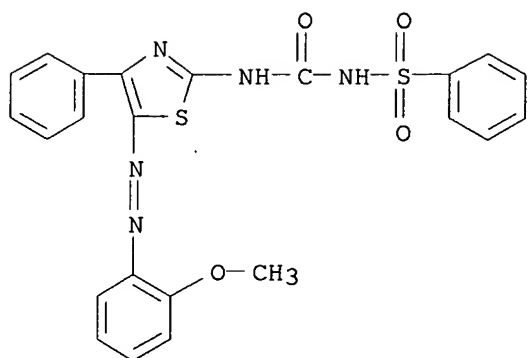
RN 107605-28-7 CAPLUS

CN Benzenesulfonamide, N-[[[5-[(2-nitrophenyl)azo]-4-phenyl-2-thiazolyl]amino]carbonyl]- (9CI) (CA INDEX NAME)

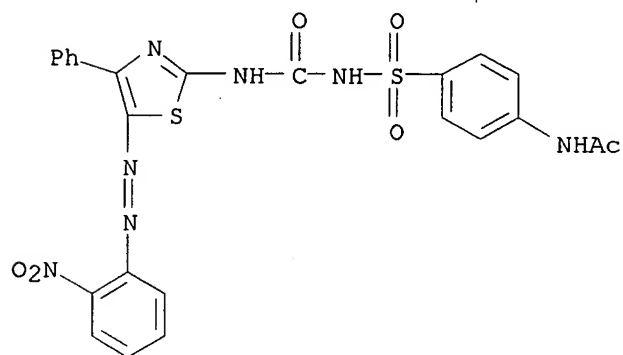


RN 107605-29-8 CAPLUS

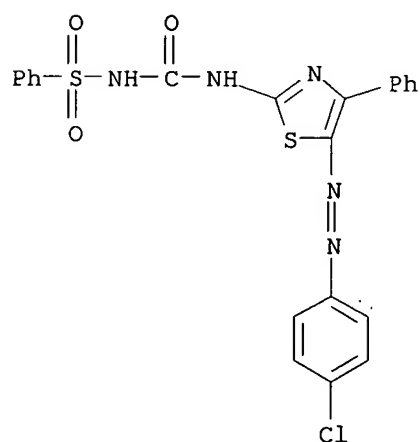
CN Benzenesulfonamide, N-[[[5-[(2-methoxyphenyl)azo]-4-phenyl-2-thiazolyl]amino]carbonyl]- (9CI) (CA INDEX NAME)



RN 107633-71-6 CAPLUS  
 CN Acetamide, N-[4-[[[5-[(2-nitrophenyl)azo]-4-phenyl-2-thiazolyl]amino]carbonyl]amino]sulfonyl]phenyl]- (9CI) (CA INDEX NAME)



RN 107633-94-3 CAPLUS  
 CN Benzenesulfonamide, N-[[[5-[(4-chlorophenyl)azo]-4-phenyl-2-thiazolyl]amino]carbonyl]- (9CI) (CA INDEX NAME)

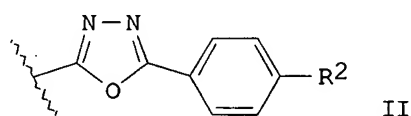
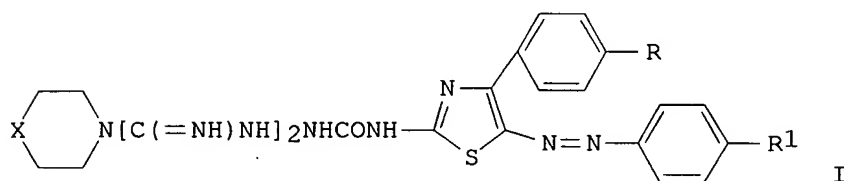


L16 ANSWER 3 OF 15 CAPLUS COPYRIGHT 2007 ACS on STN  
 AN 1985:6411 CAPLUS  
 DN 102:6411  
 TI Synthesis of 4-methyl-1-piperazino/piperidinobiguanides as oral



hypoglycemic agents

AU Husain, M. I.; Srivastava, V. P.  
CS Dep. Chem., Lucknow Univ., Lucknow, 226 007, India  
SO Indian Journal of Chemistry, Section B: Organic Chemistry Including  
Medicinal Chemistry (1984), 23B(8), 789-92  
CODEN: IJSBDB; ISSN: 0376-4699  
DT Journal  
LA English  
OS CASREACT 102:6411  
GI

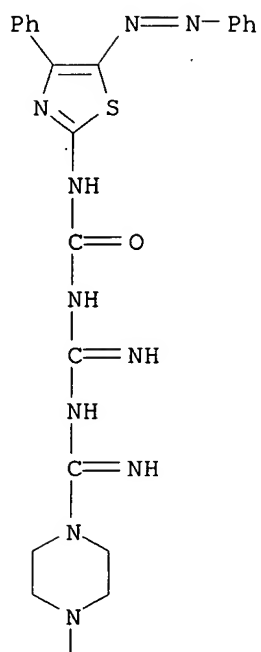


AB Piperidinobiguanides I and II (X = NMe, CH<sub>2</sub>; R = H, Cl; R<sub>1</sub> = H, Me, Cl; R<sub>2</sub> = H, Me, OMe, NMe<sub>2</sub>, NO<sub>2</sub>) have been synthesized from N5-ethoxycarbonyl analogs. The latter compds. in turn have been prepared by the reaction of N1-substituted biguanide hydrochlorides with ClCO<sub>2</sub>Et. A few compds. of the series, when administered orally in rats, cause reduction in the blood sugar to a significant extent but most of these have been found to be toxic.

IT 93546-50-0P 93546-51-1P 93546-52-2P  
93546-53-3P 93546-54-4P 93546-55-5P  
93546-56-6P 93546-57-7P 93546-58-8P  
93546-59-9P 93546-60-2P 93546-61-3P  
RL: BAC (Biological activity or effector, except adverse); BSU (Biological study, unclassified); SPN (Synthetic preparation); THU (Therapeutic use); BIOL (Biological study); PREP (Preparation); USES (Uses)  
(preparation and antidiabetic activity of)

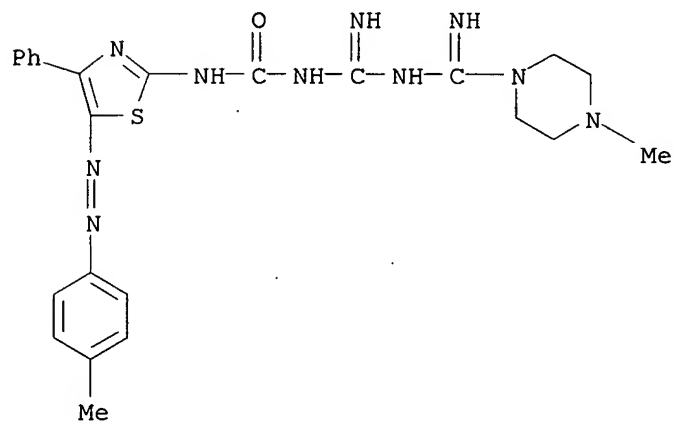
RN 93546-50-0 CAPLUS

CN 1-Piperazinecarboximidamide, N-[imino[[[4-phenyl-5-(phenylazo)-2-thiazolyl]amino]carbonyl]amino]methyl]-4-methyl- (9CI) (CA INDEX NAME)



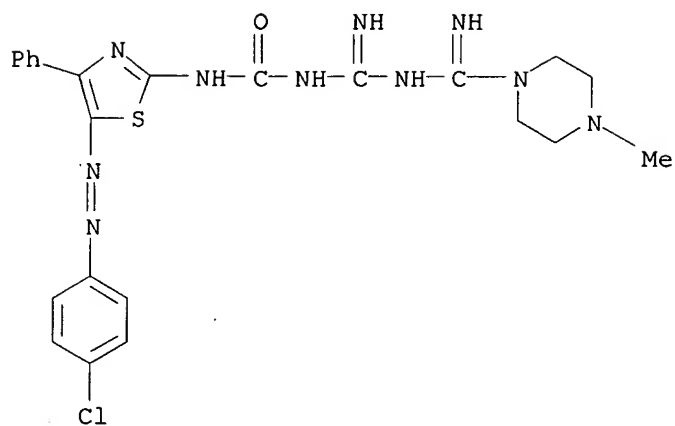
RN 93546-51-1 CAPLUS

CN 1-Piperazinecarboximidamide, N-[imino[[[5-[(4-methylphenyl)azo]-4-phenyl-2-thiazolyl]amino]carbonyl]amino]methyl]-4-methyl- (9CI) (CA INDEX NAME)



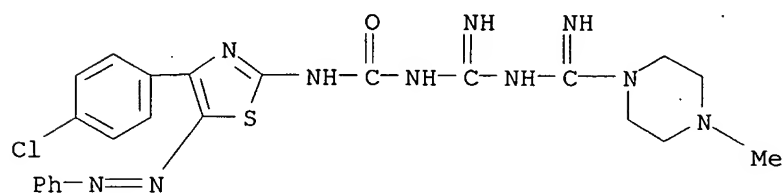
RN 93546-52-2 CAPLUS

CN 1-Piperazinecarboximidamide, N-[[[[5-[(4-chlorophenyl)azo]-4-phenyl-2-thiazolyl]amino]carbonyl]amino]iminomethyl]-4-methyl- (9CI) (CA INDEX NAME)



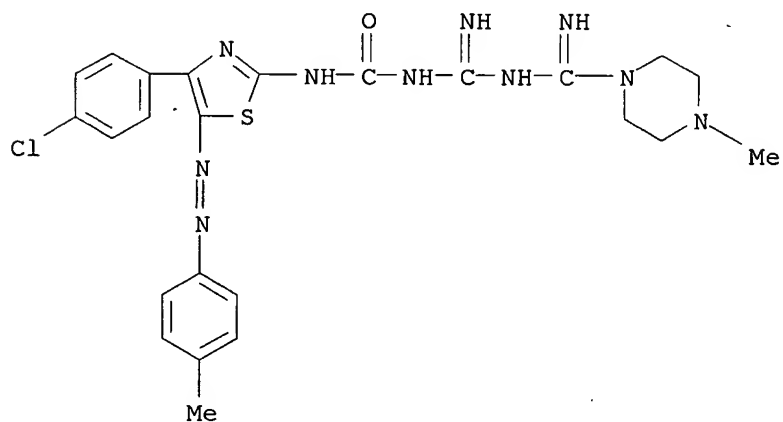
RN 93546-53-3 CAPLUS

CN 1-Piperazinecarboximidamide, N-[[[4-(4-chlorophenyl)-5-(phenylazo)-2-thiazolyl]amino]carbonyl]amino]iminomethyl]-4-methyl- (9CI) (CA INDEX NAME)



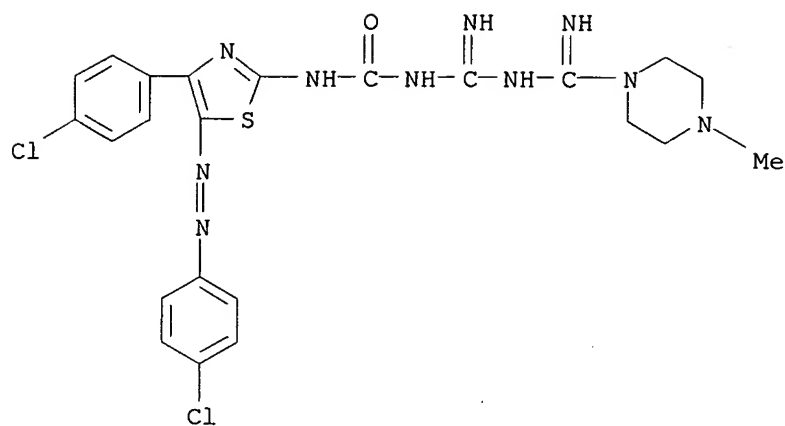
RN 93546-54-4 CAPLUS

CN 1-Piperazinecarboximidamide, N-[[[4-(4-chlorophenyl)-5-[(4-methylphenyl)azo]-2-thiazolyl]amino]carbonyl]amino]iminomethyl]-4-methyl- (9CI) (CA INDEX NAME)



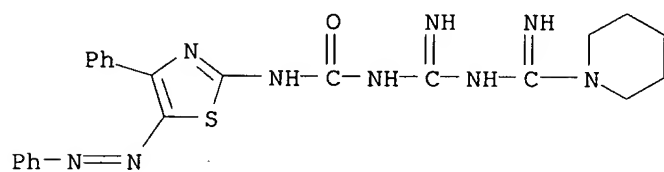
RN 93546-55-5 CAPLUS

CN 1-Piperazinecarboximidamide, N-[[[4-(4-chlorophenyl)-5-[(4-chlorophenyl)azo]-2-thiazolyl]amino]carbonyl]amino]iminomethyl]-4-methyl- (9CI) (CA INDEX NAME)



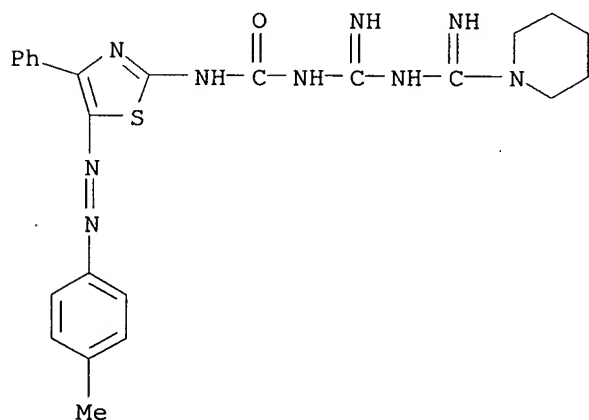
RN 93546-56-6 CAPLUS

CN 1-Piperidinecarboximidamide, N-[imino[[[4-phenyl-5-(phenylazo)-2-thiazolyl]amino]carbonyl]amino]methyl]- (9CI) (CA INDEX NAME)



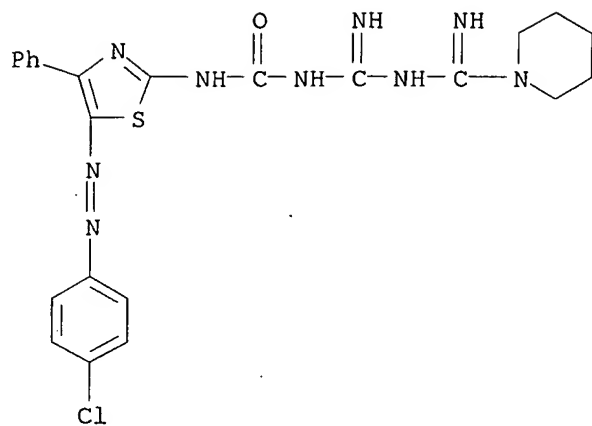
RN 93546-57-7 CAPLUS

CN 1-Piperidinecarboximidamide, N-[imino[[[5-[(4-methylphenyl)azo]-4-phenyl-2-thiazolyl]amino]carbonyl]amino]methyl]- (9CI) (CA INDEX NAME)



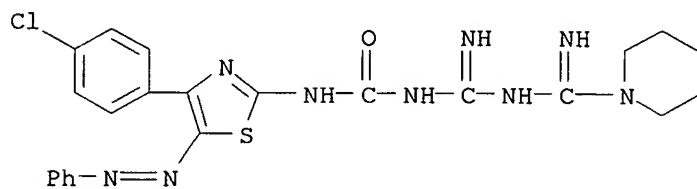
RN 93546-58-8 CAPLUS

CN 1-Piperidinecarboximidamide, N-[[[[5-[(4-chlorophenyl)azo]-4-phenyl-2-thiazolyl]amino]carbonyl]amino]iminomethyl]- (9CI) (CA INDEX NAME)



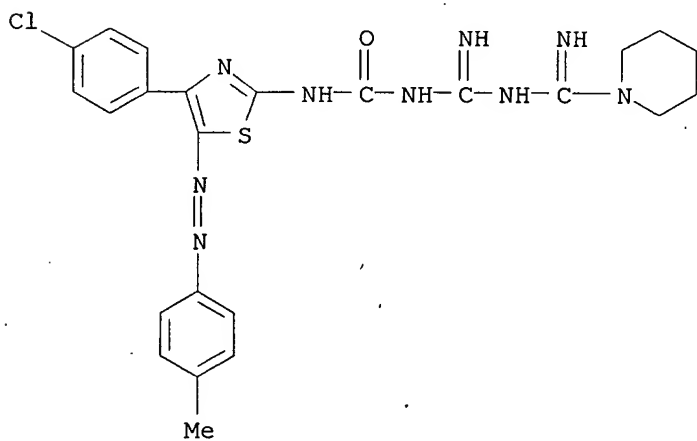
RN 93546-59-9 CAPLUS

CN 1-Piperidinecarboximidamide, N-[[[4-(4-chlorophenyl)-5-(phenylazo)-2-thiazolyl]amino]carbonyl]amino]iminomethyl]- (9CI) (CA INDEX NAME)



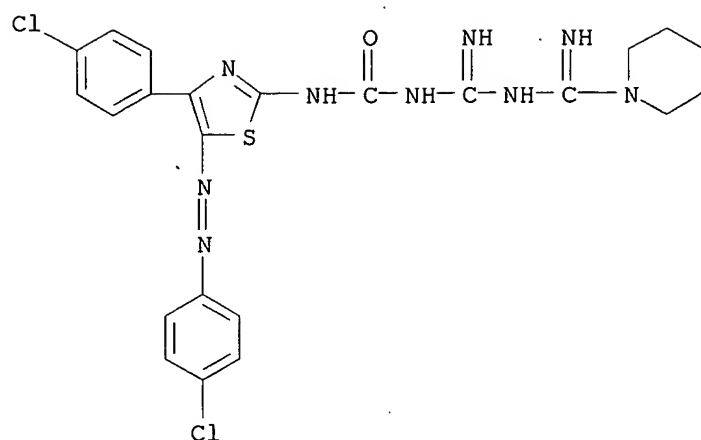
RN 93546-60-2 CAPLUS

CN 1-Piperidinecarboximidamide, N-[[[4-(4-chlorophenyl)-5-[(4-methylphenyl)azo]-2-thiazolyl]amino]carbonyl]amino]iminomethyl]- (9CI) (CA INDEX NAME)

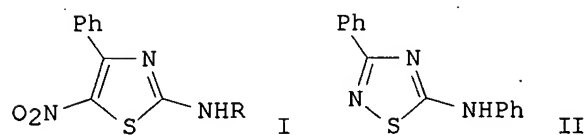


RN 93546-61-3 CAPLUS

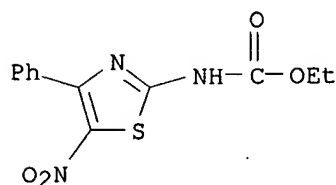
CN 1-Piperidinecarboximidamide, N-[[[4-(4-chlorophenyl)-5-[(4-chlorophenyl)azo]-2-thiazolyl]amino]carbonyl]amino]iminomethyl]- (9CI) (CA INDEX NAME)



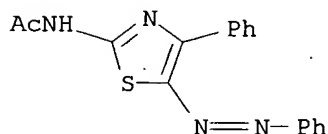
L16 ANSWER 4 OF 15 CAPLUS COPYRIGHT 2007 ACS on STN  
 AN 1979:152059 CAPLUS  
 DN 90:152059  
 TI A novel synthesis of thiazoles: Part II. Synthesis of  
 2-amino-5-nitrothiazoles by direct ring-closure reactions  
 AU Rajappa, S.; Advani, B. G.  
 CS Ciba-Geigy Res. Cent., Bombay, India  
 SO Indian Journal of Chemistry, Section B: Organic Chemistry Including  
 Medicinal Chemistry (1978), 16B(9), 749-51  
 CODEN: IJSBDB; ISSN: 0376-4699  
 DT Journal  
 LA English  
 OS CASREACT 90:152059  
 GI



AB Cyclocondensation of  $\text{H}_2\text{NCPh:NCSNHPh}$  with  $\text{BrCH}_2\text{NO}_2$  in refluxing  $\text{Me}_2\text{CHOH}$   
 gave only 8.6% thiazole I ( $\text{R} = \text{Ph}$ ) and mostly thiadiazole II, whereas  
 similar cyclization of  $\text{Et}_2\text{NPh:NCSNHPh}$  gave 37% I ( $\text{R} = \text{Ph}$ ). I ( $\text{R} =$   
 4- $\text{ClC}_6\text{H}_4$ , Me,  $\text{PhCH}_2$ , allyl, Me $_3\text{C}$ , cyclohexyl,  $\text{EtO}_2\text{C}$ ) were also prepared by  
 cyclization of  $\text{Et}_2\text{NPh:NCSNHR}$ .  
 IT 69818-64-0P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (preparation of)  
 RN 69818-64-0 CAPLUS  
 CN Carbamic acid, (5-nitro-4-phenyl-2-thiazolyl)-, ethyl ester (9CI) (CA  
 INDEX NAME)



L16 ANSWER 5 OF 15 CAPLUS COPYRIGHT 2007 ACS on STN  
 AN 1973:71980 CAPLUS  
 DN 78:71980  
 TI Azo derivatives of heterocycles. I. New azo derivatives of thiazole and benzothiazole  
 AU Fedorova, L. N.; Pochinok, V. Ya.; Rozum, Yu. S.  
 CS USSR  
 SO Khim. Geterotsikl. Soedin., Sb. 3 (1971), No. 3, 182-9  
 From: Ref. Zh., Khim. 1972, Abstr. No. 6Zh509  
 DT Journal  
 LA Russian  
 GI For diagram(s), see printed CA Issue.  
 AB Coupling the diazonium salts of 2-methylbenzothiazoles with the appropriate 2-aminothiazoles gave I (R and % yield given): Me, 70; Ph, 82; p-tolyl, 86; p-MeOC6H4, 72; p-ClC6H4, 91; p-BrC6H4, 89; and II (same data given): Me, 78; Ph, 96; p-tolyl, 85; p-MeOC6H4, 74; p-ClC6H4, 88; and p-BrC6H4, 91. Coupling 2-amino-4,5-dimethylthiazole with the appropriate diazonium salt gave III (R and % yield given): H, 82; Me, 80; NO2, 98; SO3Na, 23. Similarly prepared were IV (R, R1, and % yield given): NH2, Me, 80; HN2, Ph, 77.5; NHAc, Ph, 61.  
 IT 40671-16-7P  
 RL: SPN (Synthetic preparation); PREP (Preparation) (preparation of)  
 RN 40671-16-7 CAPLUS  
 CN Acetamide, N-[4-phenyl-5-(phenylazo)-2-thiazolyl]- (9CI) (CA INDEX NAME)



L16 ANSWER 6 OF 15 CAPLUS COPYRIGHT 2007 ACS on STN

AN 1963:441732 CAPLUS

DN 59:41732

OREF 59:7534e-h

TI Acyl derivatives of 2-amino-5-nitrothiazole

IN Chanterreau, Henri R.

SO 14 pp.

DT Patent

LA Unavailable

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	FR M716		19610904	FR	19600805 <--
PRAI	FR		19600805		

OS MARPAT 59:41732

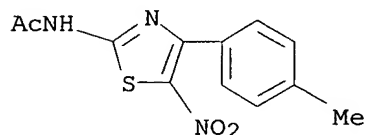
GI For diagram(s), see printed CA Issue.

AB Title compds. (I) were prepared by catalyzed nitration with HNO3H2SO4 or HNO3-HF of II or, alternatively, by treating (III) with RCOCl or (RCO)2O in the presence of bases. Thus, 15.5 g. 2-thenoyl chloride was added to 23.5 g. III (R1 = p-tolyl) in 25 cc. C5H5N (cooling), the mixture stirred 1 hr., and poured onto ice, and the precipitate filtered off, dried, and recrystd.

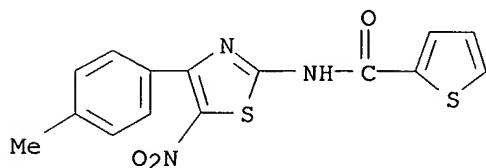
from Me2CO to give I (R = 2-thenoyl, R1 = p-tolyl), m. 2422. Similarly prepared were the following I (R1 = H; R and m.p. given): 4-nitro-2-thienyl, 165°; 5-nitro-2-thienyl, 190°; p-nitrophenyl, 272°; o-tolyl, 228°; o-methoxyphenyl, 259° (in this case the acid

anhydride was used). A suspension of 14.5 g. III (R1 = H), 11.8 g. furoic acid, 3 cc. piperidine, an 100 cc. PhMe, was treated on a water bath with 13 g. purified SOCl<sub>2</sub>, the mixture refluxed 1 hr., cooled, and poured on ice, and the precipitate filtered off and recrystd. from dioxane to give I (R = 2-furyl, R1 = H), m.274. By the same method were prepared the following I (R1 = H; R and m.p. given): p-methoxyphenyl, 234°; 3,4-dichlorophenyl, 217°. I (R = Ac, R1 = p-tolyl) (IV) was prepared by treating, at -15, 2.5 g. 2-acetamido-4-(p-tolyl)thiazole in 10 cc. H<sub>2</sub>SO<sub>4</sub> containing 0.25 g. Cu(NO<sub>3</sub>), with a mixture of 4 cc. HNO<sub>3</sub> (d 1.49) and 5 cc. H<sub>2</sub>AO1. After 15 min., the mixture was poured onto ice, filtered, and the precipitate recrystd. from EtOH to give IV, m. 251°. A solution of 2 g. II (R = Ac, R1 = p-hexadecylphenyl) (m. 143) in 15cc. HF containing 2 g. NaNO<sub>3</sub>, was treated (with stirring, -20°) with 4 cc. HNO<sub>3</sub> (d. 1.48). Work up as in the last example gave the corresponding I, m. 183°. The following I were prepared (R1 = H; R and m.p. given): m-methoxyphenyl, 226°; 2,4-dichlorophenyl, 206°; m-tolyl, 227°. The compds. are active against *Trichomonas vaginalis*.

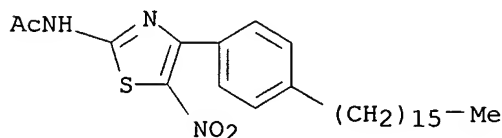
IT 91397-48-7P, Thiazole, 2-acetamido-5-nitro-4-p-tolyl-  
 92849-82-6P, 2-Thiophenecarboxamide, N-(5-nitro-4-p-tolyl-2-thiazolyl)-  
 96973-78-3P, Thiazole, 2-acetamido-4-(p-hexadecylphenyl)-5-nitro-  
 RL: PREP (Preparation)  
 (preparation of)  
 RN 91397-48-7 CAPLUS  
 CN Thiazole, 2-acetamido-5-nitro-4-p-tolyl- (6CI, 7CI) (CA INDEX NAME)



RN 92849-82-6 CAPLUS  
 CN 2-Thiophenecarboxamide, N-(5-nitro-4-p-tolyl-2-thiazolyl)- (7CI) (CA INDEX NAME)



RN 96973-78-3 CAPLUS  
 CN Thiazole, 2-acetamido-4-(p-hexadecylphenyl)-5-nitro- (6CI, 7CI) (CA INDEX NAME)





DN 58:73349  
 OREF 58:12569b-d  
 TI 2-Acylamino-5-nitrothiazoles  
 PA Innothera and Nguyen Dat Xuong  
 SO 12 pp.  
 DT Patent  
 LA Unavailable  
 FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	FR 1306603		19621019	FR 1958-772539	19580814 <--
PRAI	FR		19580814		

GI For diagram(s), see printed CA Issue.

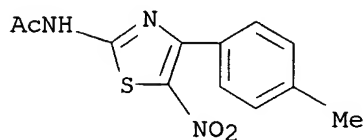
AB The title compds. with or without alkyl or aryl in position 4 are prepared by nitrating the 2-acylaminothiazoles or by acylating the 2-amino-5-nitrothiazoles. Thus, 2-isobutyramido-5-nitrothiazole was obtained by adding dropwise 29 g. 2-amino-5-nitrothiazole in 50 ml. dry C<sub>5</sub>H<sub>5</sub>N to 35 g. isobutyric anhydride at 5-10°. The mixture was kept 2 hrs. at room temperature, then poured onto 200 g. ice, and recrystd. from Me<sub>2</sub>CO or dioxane, yellow, m. 212°. Similarly prepared were:  
 2- $\alpha$ -furoylamino-5-nitrothiazole (I), yellow, m. 274°;  
 2-(4-nitro-2-thenoylamino)-5-nitrothiazole, red, m. 165°;  
 2-carbethoxyformamido-5-nitrothiazole, yellow, m. 248°;  
 2-(5-nitro-2-thenoylamino)-5-nitrothiazole, red orange, m. 190°;  
 2-p-nitrobenzamido-5-nitrothiazole, orange, m. 272°;  
 2-p-methoxybenzamido-5-nitrothiazole, m. 234°; 2-(3,4-dichlorobenzamido)-5-nitrothiazole, m. 217°; 2-o-methylbenzamido-5-nitrothiazole, yellow, m. 228°;  
 4-p-tolyl-2-acetamido-5-nitrothiazole, yellow, m. 251°;  
 4-(p-hexadecylphenyl)-2-acetamido-5-nitrothiazole, yellow, m. 184°;  
 2-(o-methoxybenzamido)-5-nitrothiazole, yellow, m. 259°;  
 2-m-methoxybenzamido-5-nitrothiazole, m. 226°; 2-(2,4-dichlorobenzamido)-5-nitrothiazole, yellow, m. 206°;  
 2-m-methylbenzamido-5-nitrothiazole, yellow, m. 227°.

IT 91397-48-7P, Thiazole, 2-acetamido-5-nitro-4-p-tolyl-  
 92849-82-6P, 2-Thiophenecarboxamide, N-(5-nitro-4-p-tolyl-2-thiazolyl)- 96973-78-3P, Thiazole, 2-acetamido-4-(p-hexadecylphenyl)-5-nitro-  
 RL: PREP (Preparation)

(preparation of)

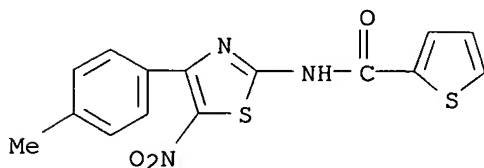
RN 91397-48-7 CAPLUS

CN Thiazole, 2-acetamido-5-nitro-4-p-tolyl- (6CI, 7CI) (CA INDEX NAME)

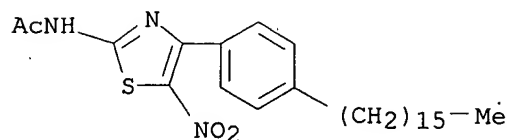


RN 92849-82-6 CAPLUS

CN 2-Thiophenecarboxamide, N-(5-nitro-4-p-tolyl-2-thiazolyl)- (7CI) (CA INDEX NAME)



RN 96973-78-3 CAPLUS  
 CN Thiazole, 2-acetamido-4-(p-hexadecylphenyl)-5-nitro- (6CI, 7CI) (CA INDEX NAME)



L16 ANSWER 8 OF 15 CAPLUS COPYRIGHT 2007 ACS on STN

AN 1959:77770 CAPLUS

DN 53:77770

OREF 53:14089b-i

TI The amino and sulfanilamido derivatives of new 4-arylthiazoles

AU Buu-Hoi, Ng. Ph.; Petit, L.; Xuong, N. D.

CS Inst. Radium, Paris

SO Bulletin de la Societe Chimique de France (1958) 1437-40

CODEN: BSCFAS; ISSN: 0037-8968

DT Journal

LA Unavailable

OS CASREACT 53:77770

AB 4-Aryl-2-aminothiazole derivs. containing liposol. groups were prepared for biol. testing for antituberculosis activity by 2 methods. Method A: 0.2 mole ArCOMe, 0.4 mole (H2N)2CS, and 0.2 mole iodine was heated 12 hrs. in a closed vessel at 100°, H2O added, the mixture cooled, made alkaline with NH4OH, and extracted with Et2O, the extract washed with H2O, dried over CaCl2, evaporated and crystallized Method B: ArCOCH2Br was refluxed 3 hrs.

with

1.5 moles (H2N)2CS in alc., the mixture cooled, 15% NaOH solution added, and the precipitate washed with H2O, dried and crystallized Method A gave good results

when Ar was simple, and especially with fragile ketones, but the yield decreased as the length of side chain increased; B gave much better yields in the latter case. RCH2Ph (0.1 mole) in 150 ml. dry CS2 at 0°, 14 g. finely powdered AlCl3, and 0.1 mole AcCl left overnight at room

temperature, the

mixture heated on the steam bath, decomposed by ice and HCl, and the organic layer washed with N NaOH and H2O, dried over CaCl2, distilled in vacuo and crystallized from EtOH gave the following acetophenones (yield in g., m.p., bn, and n in mm. given): p-decyl, 11.2, 38°, 195-8°, 18; p-dodecyl, 18, 40°, 211-14°, 15; p-hexadecyl, 20.6, 60°, 243-6°, 16. The Br derivs. used for method B were prepared in mediocre yield by action of the theoretical amount of Br on the acetophenones in CHCl3. The following 4-Ar-substituted-2-aminothiazoles were prepared (Ar, m.p., crystallizing solvent, % yield by method A, and %

yield

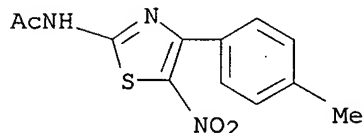
by method B, if used, given): p-tolyl (I), 132°, cyclohexane, 50; cumyl, 115°, AcOEt, 40; 1,2,3,4-tetrahydro-2-naphthyl, 101°, cyclohexane, 75; 2-thienyl, 117°, AcOEt, 62; p-heptylphenyl, 84°, petr. ether, 30, 55; p-decylphenyl, 80°, cyclohexane-petr. ether, 24, 48; p-dodecylphenyl, 76°, cyclohexane, 20, 40; p-tetradecylphenyl, 74°, cyclohexane, 16; p-hexadecylphenyl (II), 72°, cyclohexane, 10, 84. An equimolar amount of Ac2O added to I in anhydrous C5H5N, and the product poured into excess dilute HCl yielded 90% 4-(p-tolyl)-2-acetamidothiazole, m. 213° (EtOH), which on nitration (C.A. 40, 37211) yielded 73% 4-(p-tolyl)-2-acetamido-5-nitrothiazole, m. 250° (EtOH). Similarly treated, II yielded 95% 4-(p-hexadecylphenyl)-2-acetamidothiazole, m. 143°, and

subsequently 84% 5-nitro derivative, m. 183°. AcNHC6H4SO2Cl (0.1 mole) in dry C5H5N added to 0.1 mole 4-Ar-substituted-2-aminothiazole in 15 ml. C5H5N, the mixture heated 20 min. to 70-80°, cooled, and poured into excess dilute HCl and ice yielded 75-85% of the following 2-(N4-acetylsulfanilamido)-4-Ar-substituted-thiazoles (Ar and m.p. given): p-tolyl, 171°; p-isopropylphenyl, 158°; 1,2,3,4-tetrahydro-2-naphthyl, 166°; p-heptylphenyl, 173°; p-decylphenyl, 170°; p-dodecylphenyl, 169°; p-tetradecylphenyl, 166°; p-hexadecylphenyl, 166°; 2-thienyl (III), 160°.

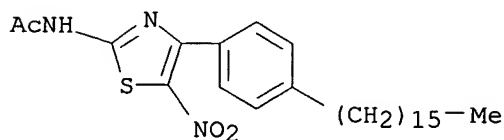
These compds. refluxed 4 hrs. with 20 ml. concentrated HCl in EtOH and the mixture

neutralized with NaHCO3 yielded 60-80% of the following 2-sulfanilamido-4-Ar-substituted-thiazoles (Ar and m.p. given): p-tolyl, 215°; p-isopropylphenyl, 189°; 1,2,3,4-tetrahydro-2-naphthyl, 256°; p-heptylphenyl, 220°; p-decylphenyl, 214°; p-dodecylphenyl, 198°; p-tetradecylphenyl, 197°; p-hexadecylphenyl, 192°. III was unstable and could not be deacetylated. 2-Amino-3-ethyl-6-methylpyridine (from NaNH2 and 3-ethyl-6-methylpyridine) with AcNHC6H4SO2Cl as above gave 2-(N4-acetylsulfanilamido)-3-ethyl-6-methylpyridine, m. 186°, which on deacetylation gave 2-sulfanilamido-3-ethyl-6-methylpyridine, m. 290°. 2-(N4-Acetylsulfanilamido)-6-phenethylpyridine, m. 172°, and 2-sulfanilamido-6-phenethylpyridine, m. 278°, were similarly prepared

IT 91397-48-7P, Thiazole, 2-acetamido-5-nitro-4-p-tolyl-  
96973-78-3P, Thiazole, 2-acetamido-4-(p-hexadecylphenyl)-5-nitro-  
RL: PREP (Preparation)  
(preparation of)  
RN 91397-48-7 CAPLUS  
CN Thiazole, 2-acetamido-5-nitro-4-p-tolyl- (6CI, 7CI) (CA INDEX NAME)



RN 96973-78-3 CAPLUS  
CN Thiazole, 2-acetamido-4-(p-hexadecylphenyl)-5-nitro- (6CI, 7CI) (CA INDEX NAME)



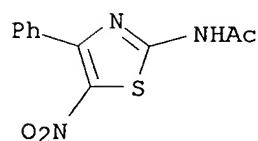
L16 ANSWER 9 OF 15 CAPLUS COPYRIGHT 2007 ACS on STN  
AN 1956:38430 CAPLUS  
DN 50:38430  
OREF 50:7467a-i,7468a-i,7469a-b  
TI 2-[p-(Fluoroalkylamino)phenylazo]-5-nitrothiazoles  
IN Dickey, Joseph B.; Towne, Edmund B.  
PA Eastman Kodak Co.  
DT Patent  
LA Unavailable  
FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
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PI	US 2730523		19560110	US 1952-304837	19520816 <--
GI	For diagram(s), see printed CA Issue.				
AB	<p>The preparation is described of azo dyes of the general formula I, where X is an alkyl or alkoxy group, Y is a halogen, alkyl, or alkoxy group, Z is an alkyl or aryl group, R' is a fluorinated alkyl group, and R is alkyl, alkoxyalkyl, hydroxyalkyl, CH<sub>2</sub>CO<sub>2</sub>Me, (CH<sub>2</sub>)<sub>3</sub>CO<sub>2</sub>Me, (CH<sub>2</sub>)<sub>3</sub>CO<sub>2</sub>Bu group, etc. NaNO<sub>2</sub> (1.52 g.) added portion wise to 10 cc. concentrated H<sub>2</sub>SO<sub>4</sub> with stirring below 65°, the solution treated dropwise at 5-20° with 3 cc. EtCO<sub>2</sub>H and 17 cc. AcOH, the nitrosyl sulfuric acid mixture treated with stirring at 0-5° with 2.9 g. 2-amino-5-nitrothiazole (II) in portions and then with 20 cc. EtCO<sub>2</sub>HAcOH, stirred 3 h. at 0-5°, treated with 2 g. urea, a 10-cc. portion added with stirring at 0-5° to 0.97 g. m-MeC<sub>6</sub>H<sub>4</sub>N(CH<sub>2</sub>CH<sub>2</sub>OH)(CH<sub>2</sub>)<sub>2</sub>CF<sub>2</sub>Me (III) in 10 cc. 1:6 EtCO<sub>2</sub>HAcOH, the mixture neutralized with NaOAc to Congo red, allowed to stand 3 h., poured into cold H<sub>2</sub>O (15°), and stirred, and the precipitate washed and dried gave I with Z and X = H, Y = Me, R = CH<sub>2</sub>CH<sub>2</sub>OH, R' = (CH<sub>2</sub>)<sub>2</sub>CF<sub>2</sub>Me. This compound dyed cellulose textile materials deep, bright-blue shades of excellent fastness to gas and fairly good fastness to light. The dyeings are dischargeable to a sharp white print. The compound also dyed wool, nylon, silk, and polyethylene terephthalate textile materials deep-blue shades. Similar dyes of the type I were prepared in the same manner from 10 cc. II diazonium solution and the following arylamines (arylamine, weight in g. used, weight in g. of the resulting azo dye, and shade of dyeing on cellulose acetate given): PhN(CH<sub>2</sub>CH<sub>2</sub>OH)(CH<sub>2</sub>)<sub>3</sub>CF<sub>2</sub>Me (IV), 0.97, 1.14, deep dark-blue; m-MeC<sub>6</sub>H<sub>4</sub>N(CH<sub>2</sub>CH<sub>2</sub>OH)(CH<sub>2</sub>)<sub>2</sub>CHF<sub>2</sub> (V), 0.92, 1.16, deep-blue; m-ClC<sub>6</sub>H<sub>4</sub>N(CH<sub>2</sub>CH<sub>2</sub>OH)(CH<sub>2</sub>)<sub>2</sub>CHF<sub>2</sub> (V), 1, 1.3, deep violet-blue. In the same manner were prepared azo dyes of the type I (aminonitrothiazole used, weight in g. used, aryl amine used, weight in g. used, weight of I obtained,</p> <p>and shade of dyeing given): II, 0.58, m-MeC<sub>6</sub>H<sub>4</sub>N(CH<sub>2</sub>CH<sub>2</sub>OH)CH<sub>2</sub>CHF<sub>2</sub> (VI), 0.86, 0.9, deep-violet; II, 0.58, m-MeC<sub>6</sub>H<sub>4</sub>N(CH<sub>2</sub>CH<sub>2</sub>OH)CH<sub>2</sub>CF<sub>3</sub> (VII), 0.93, 0.89, deep red-violet; II, 0.58, m-Me derivative of IV, 1.03, 0.66, bright blue-green; II, 0.58, PhN(CH<sub>2</sub>CH<sub>2</sub>OH)(CH<sub>2</sub>)<sub>2</sub>CHF<sub>2</sub> (VIII), 0.86, 1.04, deep-blue with a violet tint; II, 0.58, m-ClC<sub>6</sub>H<sub>4</sub>N(CH<sub>2</sub>CH<sub>2</sub>OH)(CH<sub>2</sub>)<sub>2</sub>CF<sub>2</sub>Me, 1.05, 1.14, bright-violet; II, 0.58, PhN(CH<sub>2</sub>CH<sub>2</sub>OH)CH<sub>2</sub>CHF<sub>2</sub> (IX), 0.76, 0.83, reddish violet; II, 0.58, PhN(CH<sub>2</sub>CH<sub>2</sub>OH)CH<sub>2</sub>CF<sub>3</sub> (X), 0.88, 0.87, red; II, 0.58, m-AcNH derivative (XI) of IX, 0.98, 0.64, deep-violet; 4-(m-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>) derivative (XII) of II, 1.33, m-Cl derivative of VIII, 1.25, 1.58, light-blue; XII, 1.33, III, 1.22, bright-blue; XII, 1.33, VII, 1.17, 1.52, reddish violet; XII, 1.33, VI, 1.08, 1.47, reddish violet; 4-CF<sub>3</sub> derivative (XIII) of II, 1.06, m-Me derivative of VIII, 1.15, 1.23, blue; XIII, 1.06, VI, 1.08, 1.1, violet, 4-CN derivative (XIV) of II, 1.70, m-MeC<sub>6</sub>H<sub>4</sub>N(CH<sub>2</sub>CHOHCH<sub>2</sub>OH)(CH<sub>2</sub>)<sub>2</sub>CF<sub>2</sub>Me, 2.73, -, blue; (weight of dye not given in the following); 4-Me derivative of II, 1.59, 5,2-Me(MeO)C<sub>6</sub>H<sub>3</sub>N(CH<sub>2</sub>CHOHCH<sub>2</sub>OH)(CH<sub>2</sub>)<sub>2</sub>CF<sub>2</sub>Me, 2.01, blue-violet; 4-Et derivative of II, 1.73, IX, 2.01, reddish violet; 4-Et derivative of II, 1.73, VI, 2.36, red; 4-Bu derivative (XV) of II, 2.01, PhN(CH<sub>2</sub>CHOHCH<sub>2</sub>OH)CH<sub>2</sub>CHF<sub>2</sub> (XVI), 2.11, reddish violet; XV, 2.01, m-Me derivative of XVI, 2.25, violet; 4-C<sub>6</sub>H<sub>13</sub> derivative (XVII) of II, 2.29, X, 2.19, red; XVII, 2.29, PhN(CH<sub>2</sub>CH<sub>2</sub>OH)(CH<sub>2</sub>)<sub>3</sub>CF<sub>3</sub> (XVIII), 2.47, violet; XIV, 1.70, IX, 2.01, violet-blue; XIV, 1.70, m-Cl derivative (XIX) of IX, 2.36, violet; XIII, 2.13, IX, 2.25, reddish violet; XIII, 2.13, m-Cl derivative of XVI, 2.66, red; 4-Ph derivative (XX) of II, 2.21, m-Me derivative (XXI) of XVI, 2.45, reddish blue; 4-(o-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>) derivative (XXII) of II, 2.66, IX, 2.01, blue; XXII, 2.66, m-Br derivative of IX, 2.80, blue; 4-(m-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>) derivative (XXIII) of II, 2.66, IX 2.01, blue; XXIII, 2.66, PhN(CH<sub>2</sub>CH<sub>2</sub>OH)CH<sub>2</sub>CF<sub>2</sub>Me (XXIV), 2.15, blue; 4-(p-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>) derivative (XXV) of II, 2.66, IX, 2.01, blue; XXV, 2.66,</p>				

XVI, 2.15, blue; 4-(p-ClC<sub>6</sub>H<sub>4</sub>) derivative (XXVI) of II, 2.55, X, 2.19, violet; XXVI, 2.55, m-Me derivative of X, 2.33, violet; 4-(o-BrC<sub>6</sub>H<sub>4</sub>) derivative (XXVII) of II, 2.99, IX, 2.01, violet; XXVII, 2.99, PhN(CH<sub>2</sub>CH<sub>2</sub>OH)(CH<sub>2</sub>)<sub>2</sub>CHF<sub>2</sub>, 2.15, violet-blue; 4-(o-FC<sub>6</sub>H<sub>4</sub>) derivative (XXVIII) of II, 2.39, IX, 2.01, violet; XXVIII, 2.39, PhN(CH<sub>2</sub>CH<sub>2</sub>OH)(CH<sub>2</sub>)<sub>2</sub>CF<sub>2</sub>Me, 2.29, violet; XXVIII, 2.55, X, 2.19, violet; XXVIII, 2.55, m-MeC<sub>6</sub>H<sub>4</sub>N(CH<sub>2</sub>CH<sub>2</sub>OH)(CH<sub>2</sub>)<sub>2</sub>CF<sub>3</sub> (XXIX), violet-blue; 4-(p-FC<sub>6</sub>H<sub>4</sub>) derivative (XXX) of II, 2.39, IX, 2.01, violet; XXX, 2.39, XVI, 2.31, violet; 4-(o-MeC<sub>6</sub>H<sub>4</sub>) derivative (XXXI) of II, 2.35, IX, 2.01, reddish blue; XXXI, 2.35, XIX, 2.36, violet; 4-(p-MeC<sub>6</sub>H<sub>4</sub>) derivative (XXXII) of II, 2.35, IX, 2.01, reddish blue; XXXII, 2.35, XXIX, 2.29, reddish blue; 4-(p-BuC<sub>6</sub>H<sub>4</sub>) derivative (XXXIII) of II, 2.77, IX, 2.01, violet; XXXIII, 2.77, XI, 2.58, blue; II, 1.45, N-(2-sulfoethyl)-N-(2,2-difluoroethyl)aniline, 2.65, violet; II, 1.45, N-(4-sulfobutyl)-N-(2,2-difluoroethyl)-m-toluidine; 3.07, violet. In the same manner were prepared a series of I from 1.45 g. II (arylamine, weight in g. used, and shade of dyeing given): N-(2-sulfatoethyl)-N-(2,2,2-trifluoroethyl)-m-toluidine (XXXIV), 3.13, reddish violet; N-(3-sulfatopropyl) analog of XXXIV, 3.27, reddish violet; N-(4-sulfatobutyl)-N-(2,2-difluoroethyl)-aniline (XXXV), 3.09, violet; N-(5-sulfatoamyl) analog of XXXV, 3.23, violet; N-(2-phosphatoethyl)-N-(2,2-difluoroethyl)-m-toluidine (XXXVI), 2.95, violet; N-(3-phosphatopropyl) analog of XXXVI, 3.09, violet; N-(4-phosphatobutyl)-N-(2,2,2-trifluoroethyl)aniline, 3.27, reddish violet; N-(5-phosphatoamyl)-N-(3,3,3-trifluoropropyl)aniline, 3.55, reddish blue; N-(2-phosphonoethyl)-N-(2,2-difluoroethyl)-m-chloroaniline, 2.99, red; N-(5-phosphonoamyl)-N-(2,2-difluoroethyl)aniline, 3.07, violet; m-MeC<sub>6</sub>H<sub>4</sub>N(CH<sub>2</sub>CO<sub>2</sub>Me)CH<sub>2</sub>CHF<sub>2</sub>, 2.43, red; m-MeC<sub>6</sub>H<sub>4</sub>N(CH<sub>2</sub>CO<sub>2</sub>Me)CH<sub>2</sub>CF<sub>2</sub>Me, 2.71, red; PhN(CH<sub>2</sub>CO<sub>2</sub>Bu)CH<sub>2</sub>CHF<sub>2</sub>, 2.71, red; m-MeC<sub>6</sub>H<sub>4</sub>N(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>Bu)CH<sub>2</sub>CHF<sub>2</sub>, 2.99, red; m-MeC<sub>6</sub>H<sub>4</sub>N(CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>Me)CH<sub>2</sub>CF<sub>3</sub>, 2.75, red; m-MeC<sub>6</sub>H<sub>4</sub>N(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>Me)CH<sub>2</sub>CF<sub>3</sub>, 2.89, red; PhN(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>Et)CH<sub>2</sub>CHF<sub>2</sub>, 2.71, red; m-MeC<sub>6</sub>H<sub>4</sub>N(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>Bu)CH<sub>2</sub>CHF<sub>2</sub>, 2.99, red; m-MeC<sub>6</sub>H<sub>4</sub>NPrCH<sub>2</sub>CHF<sub>2</sub>, 2.13, reddish blue; PhN(CHMe<sub>2</sub>)CH<sub>2</sub>CF<sub>2</sub>Me, 2.13, reddish blue; m-MeC<sub>6</sub>H<sub>4</sub>NBuCH<sub>2</sub>CF<sub>3</sub>, 2.45, reddish violet; PhN(C<sub>6</sub>H<sub>13</sub>)CH<sub>2</sub>CF<sub>3</sub>, 2.59, reddish violet; PhN(C<sub>10</sub>H<sub>21</sub>)CH<sub>2</sub>CHF<sub>2</sub>, 2.97, reddish violet; PhN(C<sub>8</sub>H<sub>17</sub>)CH<sub>2</sub>CHF<sub>2</sub>, 2.69, reddish blue; m-MeC<sub>6</sub>H<sub>4</sub>N(CH<sub>2</sub>CH<sub>2</sub>OMe)CH<sub>2</sub>CHF<sub>2</sub>, 2.29, reddish blue; PhN(CH<sub>2</sub>CH<sub>2</sub>OEt)CH<sub>2</sub>CHF<sub>2</sub>, 2.29, reddish blue; m-MeC<sub>6</sub>H<sub>4</sub>N(CH<sub>2</sub>CH<sub>2</sub>OPr)CH<sub>2</sub>CHF<sub>2</sub>, 2.57, reddish blue; PhN(CH<sub>2</sub>CH<sub>2</sub>OBu)CH<sub>2</sub>CHF<sub>2</sub>, 2.57, reddish blue; m-MeC<sub>6</sub>H<sub>4</sub>N(CH<sub>2</sub>CF<sub>3</sub>)CH<sub>2</sub>CH(OH)Me, 2.47, reddish blue; m-MeC<sub>6</sub>H<sub>4</sub>N(CH<sub>2</sub>CF<sub>3</sub>)(CH<sub>2</sub>)<sub>3</sub>OH, 2.47, reddish blue; XXI, 2.45, reddish blue; m-MeC<sub>6</sub>H<sub>4</sub>N(CH<sub>2</sub>CHF<sub>2</sub>)(CH<sub>2</sub>)<sub>4</sub>OH, 2.43, reddish blue; PhN(CH<sub>2</sub>CHF<sub>2</sub>)(CH<sub>2</sub>)<sub>5</sub>OH, 2.43, reddish blue; PhN(CH<sub>2</sub>CHF<sub>2</sub>)CH<sub>2</sub>CH<sub>2</sub>CN, 2.10, red; m-MeC<sub>6</sub>H<sub>4</sub>N(CH<sub>2</sub>CHF<sub>2</sub>)(CH<sub>2</sub>)<sub>3</sub>CN, 2.38, red; m-MeC<sub>6</sub>H<sub>4</sub>N(CH<sub>2</sub>CHF<sub>2</sub>)(CH<sub>2</sub>)<sub>4</sub>CN, 2.70, red; PhN(CH<sub>2</sub>CF<sub>3</sub>)(CH<sub>2</sub>)<sub>5</sub>CN, red; PhN(CH<sub>2</sub>CH<sub>2</sub>OH)(CH<sub>2</sub>)<sub>2</sub>CHF<sub>2</sub>, 2.15, reddish blue; XXIV, 2.29, bluish red; V, 2.43, blue; PhN(CH<sub>2</sub>CH<sub>2</sub>OH)(CH<sub>2</sub>)<sub>3</sub>CF<sub>2</sub>Me, 2.43, blue; PhN(CH<sub>2</sub>CH<sub>2</sub>OH)(CH<sub>2</sub>)<sub>2</sub>CF<sub>3</sub>, 2.33, blue; m-Me derivative of XVIII, 2.61, blue; o-Me derivative of IX, 2.15, red; o-Et derivative of IX, 2.29, red; o-MeO derivative of IX, 2.31, red; o-EtO derivative of IX, 2.45; red; o-Cl derivative of X, 2.54, red; o-Br derivative of X, 2.98, red; m-Et derivative of IX, 2.29, bluish red; m-Et derivative of X, 2.47, reddish violet; m-MeO derivative of IX, 2.31, bluish red; m-MeO derivative of IX, 2.49, reddish violet; XIX, 2.35, reddish violet; m-Cl derivative of X, 2.53, reddish violet; m-Br derivative of IX, 2.80, violet; m-Br derivative of X, 2.98, reddish violet; XI, 2.58, blue; m-EtCONH derivative of IX, 2.72, blue; m-AcNH derivative of X, 2.76, reddish blue; m-EtCONH of X, 2.90, reddish blue; m-PrCONH derivative of IX, 2.86, blue; m-PrCONH derivative of X, 3.04, reddish blue; 2,5-(MeO)<sub>2</sub> derivative of IX, 2.61, blue; 2,5-(EtO)<sub>2</sub> derivative of X, 2.79, blue; 2,5-MeO(AcNH) derivative of IX, 2.88, blue; 2,5-Cl<sub>2</sub> derivative of IX, 2.70, red; 2,5-Br<sub>2</sub> derivative of IX, 3.59,

red; 2,5-MeO(Cl) derivative of X, 2.84, reddish blue. Br (160 g.) added dropwise with stirring to 120 g. PhAc and 152 g. thiourea, the mixture heated overnight on the steam bath, diluted with 2.5 l. hot H<sub>2</sub>O (85°), stirred, and filtered hot, the filtrate cooled, made slightly basic with concentrated NH<sub>4</sub>OH, and filtered, and the residue recrystd. from EtOH gave 126 g. 2-amino-4-phenylthiazole (XXXVII), m. 144-6°. Br (160 g.), 165 g. m-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>Ac, and 152 g. thiourea gave similarly 87% m-NO<sub>2</sub> derivative (XXXVIII) of XXXVII, m. 178-80° (from EtOH). XXXVIII (60 g.) dissolved in 300 cc. H<sub>2</sub>SO<sub>4</sub> at 15°, the solution treated with 13.3 cc. fuming 90% HNO<sub>3</sub> (d. 1.5) at 10-15°, allowed to stand overnight, stirred into ice, and filtered, and the residue slurried with aqueous NaHCO<sub>3</sub> until neutral and then with H<sub>2</sub>O gave the 5-NO<sub>2</sub> derivative of XXXVIII, m. 236-7° (from PhNO<sub>2</sub>). XXXVII (15 g.) heated on a steam bath with 50 cc. Ac<sub>2</sub>O, cooled, poured into H<sub>2</sub>O, stirred, and filtered gave the N-acetyl derivative (XXXIX) of XXXVII, m. 206-8° (from EtOH). XXXIX nitrated in the usual manner with H<sub>2</sub>SO<sub>4</sub> and fuming HNO<sub>3</sub>, and the resulting 5-NO<sub>2</sub> derivative, m. 215-24°, 7 g., hydrolyzed with 45 cc. HCl, 90 cc. H<sub>2</sub>O, and 90 cc. AcOH gave the 5-NO<sub>2</sub> derivative of XXXVII, m. 245-60° (from PhNO<sub>2</sub>). CF<sub>3</sub>COCH<sub>2</sub>Cl (14 g.) and 7.26 g. thiourea in 50 cc. H<sub>2</sub>O heated 4 h. on the steam bath, cooled, and made slightly alkaline with Na<sub>2</sub>CO<sub>3</sub> yielded 9.1 g. 2-amino-4-trifluoromethylthiazole (XL), m. 58-60°. XL in H<sub>2</sub>SO<sub>4</sub> nitrated at 5-10° in the usual manner with fuming HNO<sub>3</sub> gave XIII. 2-Amino-4-methylthiazole, m. 44-5°, was prepared in 70-5% yield from thiourea and AcCH<sub>2</sub>Cl.

IT 873401-60-6P, Thiazole, 2-acetamido-5-nitro-4-phenyl-  
 RL: PREP (Preparation)  
 (preparation of)  
 RN 873401-60-6 CAPLUS  
 CN Thiazole, 2-acetamido-5-nitro-4-phenyl- (5CI) (CA INDEX NAME)



L16 ANSWER 10 OF 15 CAPLUS COPYRIGHT 2007 ACS on STN  
 AN 1955:84216 CAPLUS  
 DN 49:84216  
 OREF 49:15870e-i,15871a-b  
 TI Thiazoles. XXIII. Nitrosation of 2-aminothiazoles and 3-methyl-2-imino-4-thiazolines  
 AU Beyer, Hans; Drews, Harald  
 CS Univ. Greifswald, Germany  
 SO Chemische Berichte (1954), 87, 1500-5  
 CODEN: CHBEAM; ISSN: 0009-2940  
 DT Journal  
 LA Unavailable  
 AB 2-Amino-4-phenylthiazole-HBr (I) (13 g.) in 60 cc. absolute alc. at 0° stirred 2 hrs. with 7.4 g. iso-AmONO, the clear bright red solution containing the 5-nitroso derivative reduced with 9-10 g. Zn dust and AcOH to the 5-amino derivative, the excess Zn dust and Zn(OAc)<sub>2</sub> filtered out, and 5.2 g. BzH added to the filtrate yielded 20% 2-amino-4-phenyl-5-benzalaminothiazole (II), fine yellow needles, m. 181° (from MeOH); acetate of the monoacetyl derivative, yellow needles, m. 205°. I (13g.) in 200 cc. 3N HCl at 0° stirred with 10 cc. 5N NaNO<sub>2</sub>, the 5-nitroso derivative filtered out, washed with 2N HCl, added to 80 cc. AcOH and 50 cc. EtOH, reduced as above with Zn, and BzH added yielded 15% II. II (1.4 g.) in 6 cc. C<sub>5</sub>H<sub>5</sub>N warmed a few min. with 0.7 g. BzCl and diluted with H<sub>2</sub>O gave 2-benzoylamino-4-

phenyl-5-benzalaminothiazole, intense yellow prisms, m. 198° (cf. Cook, et al., C.A. 43, 1400f) proving the constitution of II. I (13 g.) in 250 cc. H<sub>2</sub>O and 10 cc. concentrated HCl at 0°, diazotized by adding 10 cc. 5N NaNO<sub>2</sub> during 2 hrs. and treated with 150 cc. concentrated NaHSO<sub>3</sub> solution and 80 cc. concentrated HCl or 400 cc. H<sub>2</sub>O saturated with SO<sub>2</sub> and 50 cc. concentrated HCl yielded 70-80% yellow 2-amino-4-phenyl-5-nitrosothiazole-H<sub>2</sub>SO<sub>3</sub> (III) which was purified by solution in dilute NH<sub>4</sub>OH and repptn. with HCl. Similar to the formation of II from I, 2-methylamino-4-phenylthiazole treated with concentrated HCl and 5N NaNO<sub>2</sub> and the precipitated nitroso derivative treated in alc. with Zn dust and AcOH, then BzH as above gave 2-methylamino-4-phenyl-5-benzalaminothiazole, long broad needles, m. 179° (from Me<sub>2</sub>CO). But 2-imino-3-methyl-4-phenyl-4-thiazoline-HCl (11.5 g.) at 0° in 100 cc. H<sub>2</sub>O with 2 cc. N HCl and 12 cc. 5N NaNO<sub>2</sub> yielded 85% 2-nitrosoimino-3-methyl-4-phenyl-4-thiazoline (IV), yellow needles, m. 190-1° (from MeOH). IV (11 g.) in 70 cc. alc. and 80 cc. AcOH stirred at 0° with 9 g. Zn dust, gave the hydrazone in solution which with BzH gave benzaldehyde(3-methyl-4-phenyl-4-thiazolin-2-one)azine (V), shiny leaflets, m. 122° (from alc.), identical with that prepared by the reaction of MeNHCSNH<sub>2</sub>:CHPh (VI), m. 155-6° (from MeNHCSNH<sub>2</sub> and BzH in alc.), and ClCH<sub>2</sub>Bz and treating the resultant HCl salt, m. 202-3°, with concentrated NaOAc solution 2-Imino-3,4-dimethyl-4-thiazoline in 80 cc. H<sub>2</sub>O and 1 cc. 2N NaNO<sub>2</sub> gave 2-nitrosoimino-3,4-dimethyl-4-thiazoline (VII), orange-yellow needles, m. 177° (from MeOH). VII reduced to the hydrazone with Zn dust and AcOH as above, and the solution treated with BzH yielded 45% benzaldehyde(3,4-dimethyl-4-thiazolin-2-one)azine, yellow leaflets, m. 171° (from alc.), identical with that prepared from the HCl salt, m. 211-12°, prepared from heating VI and ClCH<sub>2</sub>Ac in alc. VII similarly reduced to the hydrazone and treated with AcPh gave acetophenone(3,4-dimethyl-4-thiazolin-2-one)azine, dark red prisms, m. 86°.

IT 859463-73-3P, Thiazole, 2-acetamido-5-benzylidene-amino-4-phenyl-, acetate 874508-82-4P, Thiazole, 2-benzamido-5-benzylideneamino-4-phenyl-  
 RL: PREP (Preparation)  
 (preparation of)

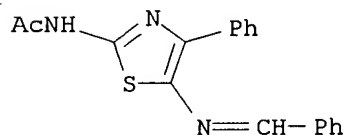
RN 859463-73-3 CAPLUS

CN Thiazole, 2-acetamido-5-benzylidene-amino-4-phenyl-, acetate (5CI) (CA INDEX NAME)

CM 1

CRN 859463-72-2

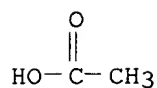
CMF C18 H15 N3 O S



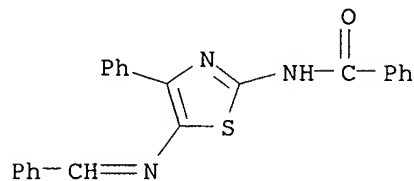
CM 2

CRN 64-19-7

CMF C2 H4 O2

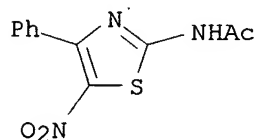


RN 874508-82-4 CAPLUS  
 CN Thiazole, 2-benzamido-5-benzylideneamino-4-phenyl- (5CI) (CA INDEX NAME)



L16 ANSWER 11 OF 15 CAPLUS COPYRIGHT 2007 ACS on STN  
 AN 1955:80926 CAPLUS  
 DN 49:80926  
 OREF 49:15248i,15249a  
 TI 2-Amino-5-nitrothiazole azo dyes  
 IN Dickey, Joseph B.; Towne, Edmund B.  
 PA Eastman Kodak Co.  
 DT Patent  
 LA Unavailable  
 FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	GB 723933		19550216	GB 1952-15713	19520623 <--
AB	See U.S. 2,659,719 (C.A. 49, 1335f).				
IT	873401-60-6, Thiazole, 2-acetamido-5-nitro-4-phenyl- (azo dyes from)				
RN	873401-60-6 CAPLUS				
CN	Thiazole, 2-acetamido-5-nitro-4-phenyl- (5CI) (CA INDEX NAME)				



L16 ANSWER 12 OF 15 CAPLUS COPYRIGHT 2007 ACS on STN  
 AN 1955:6490 CAPLUS  
 DN 49:6490  
 OREF 49:1335e-i,1336a-h  
 TI 2-Amino-5-nitrothiazole azo dyes  
 IN Dickey, Joseph B.; Towne, Edmund B.  
 PA Eastman Kodak Co.  
 DT Patent  
 LA Unavailable  
 FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 2659719		19531117	US 1951-233243	19510623 <--
GI	For diagram(s), see printed CA Issue.				
AB	2-Amino-5-nitrothiazole (I) and its derivs. are diazotized and coupled with aniline type components to give blue dyes useful for coloring				



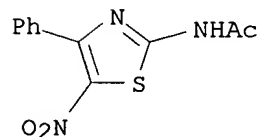
cellulose acetate. The azo compds. have the general formula A, wherein R and R' each represents an alkyl group having 1-10 C atoms, an alkoxyalkyl group of 3-6 C atoms, a hydroxyalkyl group having 2-5 C atoms, a cyanoalkyl group of 3-6 C atoms, a sulfoalkyl group of 2-4 C atoms, a sulfatoalkyl group of 2-5 C atoms, a phosphatoalkyl group of 2-5 C atoms, a phosphonoalkyl group of 2-5 C atoms, a 2-nitro-Et group, a chloroallyl group, an alkenyl group of 2-4 C atoms, or a  $(CH_2)_mCOOR''$  group (where m is a whole number selected from 1, 2, and 3 and R'' is an alkyl group of 1-4 C atoms), X represents H, an unsubstituted alkyl group of 1-6 C atoms, a cyano group, a trifluoromethyl group, or a  $C_6H_4R'''$  group (where R''' represents H, NO<sub>2</sub>, Cl, Br, F, or an alkyl group having 1-4 C atoms), Z represents an alkyl group having 1-4 C atoms, an alkoxy group of 1-4 C atoms, Cl, Br, F, or a NHCOR group (where Y represents an alkyl group having 1-3 C atoms), and n is selected from 0, 1, and 2. 12.9 g. is added at 0-5° to a nitrosyl sulfuric acid mixture made up from NaNO<sub>2</sub> 1.52, 10 cc. concentrated H<sub>2</sub>SO<sub>4</sub>, 3 cc. C<sub>2</sub>H<sub>5</sub>COOH, and 17 cc. HOAc. A mixture of 3 cc. C<sub>2</sub>H<sub>5</sub>COOH and 17 cc. HOAc is added to the diazo mixture and the whole stirred 3 h. at 0-5°, excess HNO<sub>2</sub> is removed, and the solution is added with stirring to a solution of N,N-bis(2-hydroxyethyl)-m-toluidine in 6 cc. of a 1:6 mixture of C<sub>2</sub>H<sub>5</sub>COOH-HOAc, stirred, made neutral to Congo paper with NaOAc, stirred 2-3 h., drowned in ice water, filtered, washed, and dried to yield 1.3 g. of a monoazo dye, which has affinity for cellulose acetate fabrics and colors them deep blue. Gas- and light-fastness are good. I can be dissolved in concentrated H<sub>2</sub>SO<sub>4</sub> and treated with nitrosylsulfuric acid

at

65° to give a clear diazonium solution. Diazotized I is coupled with N,N-bis(2-hydroxyethyl)-m-chloroaniline to give a deep bluish violet dye for acetate goods. Other aniline type components similarly coupled with I to give blue acetate dyes are: N-ethyl-N-(2,3-dihydroxypropyl)-m-toluidine (II), N-ethyl-N-(2-methyl-2,3-dihydroxypropyl)-m-toluidine, N-(2,3-dihydroxypropyl)-N-(2-methoxyethyl)-m-toluidine (III), N,N-bis(2-methoxyethyl)-m-toluidine, Na N-butyl-N-(2-sulfatoethyl)-m-toluidine, Na N-amyl-N-(2-sulfatopropyl)-m-ethylaniline, Na N-(2-cyanoethyl)-N-(2-phosphatoethyl)-m-chloroaniline, N,N-bis(2-hydroxyethyl)aniline (IV), N-ethyl-N-(2-sulfoethyl)aniline, N-butyl-N-(2-hydroxy-2-ethoxyethyl)aniline, N-ethyl-N-(2-hydroxyethyl)-m-toluidine, N-butyl-N-(2,3-dihydroxypropyl)-m-toluidine, N,N-bis(2-hydroxyethyl)-2-methoxy-5-chloroaniline, N-ethyl-N-(2,3-dihydroxypropyl)aniline, N-(2-hydroxyethyl)-N-(2-ethoxyethyl)aniline, N-ethyl-N-(2-hydroxyethyl)aniline, N-ethyl-N-(4,5-dihydroxyamyl)aniline, N-(2-hydroxyethyl)-N-(2-nitroethyl)aniline, N-(2-hydroxyethyl)-N-allylaniline, N-(2-carbomethoxyethyl)-N-ethylaniline, N-(3-carbomethoxypropyl)-N-(2-hydroxyethyl)-m-toluidine, N,N-bis(2-hydroxyethyl)-m-fluoroaniline, N-amyl-N-(2-hydroxyethyl)aniline, N-ethyl-N-(2-hydroxyethyl)-m-ethoxyaniline, N-decyl-N-(2-hydroxyethyl)aniline, Na N-(4-sulfatobutyl)-N-ethylaniline, Na N-(4-sulfobutyl)-N-ethylaniline, di-Na N-(2-phosphonoethyl)-N-ethylaniline, di-Na N-(2-phosphatoamyl)-N-ethylaniline, N,N-bis(2-hydroxyethyl)-m-ethoxyaniline, N,N-bis(2-hydroxyethyl)-m-acetamidoaniline, PhNEt[CH<sub>2</sub>CH<sub>2</sub>OP(=O)(OMe)<sub>2</sub>] and PhNEt[CH<sub>2</sub>CH<sub>2</sub>P(=O)(OMe)<sub>2</sub>]. Other blue dyes are prepared from diazotized: 2-amino-5-nitro-4-trifluoromethylthiazole (V) and N-methyl-N-(2,3-dihydroxypropyl)-m-toluidine, 2-amino-4-cyano-5-nitrothiazole (VI) and III, 2-amino-5-nitro-4-(m-nitrophenyl)thiazole (VII) and II, 2-amino-4-methyl-5-nitrothiazole and IV, 2-amino-4-butyl-5-nitrothiazole and N-ethyl-N-(2-hydroxyethyl)-m-bromoaniline, 2-amino-4-phenyl-5-nitrothiazole (VIII) and IV, 2-amino-4-(o-chlorophenyl)-5-nitrothiazole and IV, V and N-(2-hydroxyethyl)-N-(2-cyanoethyl)aniline, and VI and N-(2-hydroxyethyl)-N-(2-chloroallyl)aniline. VII is prepared as follows: m-Nitroacetophenone 165 is mixed with thiourea (IX) 152, treated dropwise with Br 160 parts, heated on a steam bath overnight, drowned in 4 l. hot water, clarified hot, and the filtrate cooled to give the HBr salt of

2-amino-4-(m-nitrophenyl)thiazole (X). X is converted to the free base and crystallized twice from EtOH to give 2-amino-4-(m-nitrophenyl)-thiazole (XI), m. 178-80°. XI 60 is dissolved at 15° in 300 cc. H2SO4, 13.3 cc. fuming HNO3 (90%, d. 1.5, 5% excess) is added at 10-15°, the mixture allowed to stand, drowned in ice, filtered, reslurried with NaHCO3 until neutral, washed with H2O, and crystallized from PhNO2 to give VII, m. 236-7°. 2-Amino-4-phenylthiazole (XII), m. 144-6°, is prepared similarly from acetophenone and IX. XII and (AcO)2O yield 2-acetamido-4-phenylthiazole (XIII), m. 206-8°. XIII is converted to 2-acetamido-4-phenyl-5-nitrothiazole, m. 215-24°, which is hydrolyzed in HCl-HOAc-H2O mixture to yield VIII, decompose 260°. 3-Chloro-1,1,1-trifluoro-2-propanone and IX yield 2-amino-4-trifluoromethylthiazole (XIV), m. 58-60°. XIV is nitrated to yield V. Bromopyruvonnitrile and IX similarly yield 2-amino-4-cyanothiazole which is nitrated to give VI.

IT 873401-60-6, Thiazole, 2-acetamido-5-nitro-4-phenyl-  
(azo dyes from)  
RN 873401-60-6 CAPLUS  
CN Thiazole, 2-acetamido-5-nitro-4-phenyl- (5CI) (CA INDEX NAME)



L16 ANSWER 13 OF 15 CAPLUS COPYRIGHT 2007 ACS on STN

AN 1953:65985 CAPLUS

DN 47:65985

OREF 47:11183b-h

TI Thiazoles. XI. The preparation of 2-amino-5-(phenylazo)thiazoles and the reductive scission of 2,2'-azothiazoles and 2-(phenylazo)thiazoles with phenylhydrazine

AU Beyer, Hans; Wolter, Gerhard

CS Univ. Greifswald, Germany

SO Chemische Berichte (1952), 85, 1077-83

CODEN: CHBEAM; ISSN: 0009-2940

DT Journal

LA Unavailable

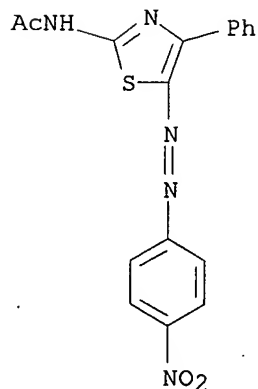
OS CASREACT 47:65985

GI For diagram(s), see printed CA Issue.

AB cf. C.A. 47, 1697a. A diazonium solution from 9.3 g. PhNH2 buffered with AcONa added at 0° to 11.4 g. 2-amino-4-methylthiazole (I) gives 90.6% 2-amino-4-methyl-5-(phenylazo)thiazole (II), p-RC6H4N:N.C:CR'.N:C(NH2).S (IIa, R = H, R' = Me), orange needles, m. 184° (di-Ac derivative, prepared by heating 1.09 g. II with 3 cc. Ac2O 1 h. on a water bath, fine yellow needles, m. 254-5°). 5-p-Tolylazo homolog (IIa, R = R' = Me), 90.5%, long dark red columns from AcOEt-Me2CO, m. 189-90°, or rhombic sepia leaflets from EtOH, m. 190-1° (di-Ac derivative, yellow needles, m. 251°); 5-p-nitrophenyl analog (IIa, R = NO2, R' = Me), 93.5%, fine dull red needles, m. 192° (di-Ac derivative, dark red leaflets, m. 206°). Coupling the diazonium compound from 17.2 g. p-H2NC6H4SO2NH2 (III) with I gives 75% p-(2-amino-4-methyl-5-thiazolylazo)benzenesulfonamide (IIa R = SO2NH2, R' = Me), m. 202° (di-Ac derivative, cubelike orange-yellow crystals, m. 223°). Coupling the diazonium salt from 9.3 g. PhNH2 with 17.6 g. 2-amino-4-phenylthiazole gives 87.8% 2-amino-4-phenyl-5-(phenylazo)thiazole (IIa, R = H, R' = Ph), fine felted cinnabar needles, m. 195° (di-Ac derivative, felted yellow needles, m. 214°);

5-p-tolylazo homolog (IIa, R = Me, R' = Ph), 71.4%, fine felted red-orange needles, m. 200° (di-Ac derivative, long felted yellow needles, m. 217°); 5-p-nitrophenyl analog (IIa, R = NO<sub>2</sub>, R' = Ph), 90.8%, fine moss-green needles, m. 254° (Ac derivative, shiny dark green crystals, m. 293°); p-(2-amino-4-phenyl-5-thiazolylazo)benzenesulfonamide (IIa R = SO<sub>2</sub>NH<sub>2</sub>, R' = Ph) 75%, bright red needles with a green surface sheen, m. 255° (di-Ac derivative, small cinnabar-red needles, m. 293°). Coupling the diazonium salt from 10.7 g. p-toluidine with 10 g. 2-aminothiazole (IV) gives 72% 2-amino-5-(p-tolylazo)thiazole (IIa, R = Me, R' = H), small fine red needles, sintering 180°, m. 205° (di-Ac derivative, dark brown powder, m. 243°); coupling the diazonium salt from 17.2 g. III with 10 g. IV gives 75% p-(2-amino-5-thiazolylazo)benzene sulfonamide (IIa, R = SO<sub>2</sub>NH<sub>2</sub>, R' = H), microcryst. brown-yellow powder, m. 223° (di-Ac derivative, yellow-brown amorphous powder, m. 235°). Azothiazoles are reductively split by PhNHNH<sub>2</sub> to the corresponding NH<sub>2</sub> compds. Heating 3.7 g. di-Et 2,2'-azobis(4-methyl-5-thiazolecarboxylate) and 10.8 g. PhNHNH<sub>2</sub> (V) slowly to 180° and keeping the mixture 5 min. at 180° and overnight at 20° give 78% Et 2-amino-4-methyl-5-thiazolecarboxylate, needles, m. 175-6°. Similarly, Et 2-phenylazo-4-methyl-5-thiazolecarboxylate and V give 90% of the 2-phenylhydrazino analog, rhombic leaflets, m. 194°, which, on further heating with V at 200° gives 72% 2-amino analog; in the same way, 2-phenylazo-4,5-diphenylthiazole gives the 2-amino compound, m. 186°. Heating 2,2'-azobis(4-phenylthiazole) or 2-phenylazo-4-phenylthiazole with V at 180° gives the corresponding hydrazo compds. which, on further heating at 220°, give 18 and 14% 2-amino-4-phenylthiazole, m. 147°.

IT 304687-35-2P, Thiazole, 2-acetamido-5-(p-nitrophenylazo)-4-phenyl-  
 RL: PREP (Preparation)  
 (preparation of)  
 RN 304687-35-2 CAPLUS  
 CN Acetamide, N-[5-[(4-nitrophenyl)azo]-4-phenyl-2-thiazolyl]- (9CI) (CA  
 INDEX NAME)



L16 ANSWER 14 OF 15 CAPLUS COPYRIGHT 2007 ACS on STN  
 AN 1949:6453 CAPLUS  
 DN 43:6453  
 OREF 43:1402d-i,1403a-i  
 TI Azole series. VIII. Interaction of  $\alpha$ -amino nitriles and carbethoxy isocyanate  
 AU Capp, C. W.; Cook, A. H.; Downer, J. D.; Heilbron, Ian  
 SO Journal of the Chemical Society (1948) 1340-5  
 CODEN: JCSOA9; ISSN: 0368-1769

DT Journal  
LA Unavailable

OS CASREACT 43:6453

AB ClCO<sub>2</sub>Et (100 cc.), added to 100 g. KSCN in 1 l. Me<sub>2</sub>CO, gives 41% EtO<sub>2</sub>CNCS (I), b<sub>18</sub> 56°. I (19.6 g.), added dropwise to H<sub>2</sub>NCH<sub>2</sub>CN in 150 cc. ether at 0°, gives 20 g. 5-amino-2-carbethoxyaminothiazole (II), m. 124°, absorption maximum (EtOH) at 2600 Å. (ε 15,500); the diazo solution yields a red precipitate with 2-ClOH<sub>7</sub>OH. II (1 g.), 2 cc. Ac<sub>2</sub>O, and

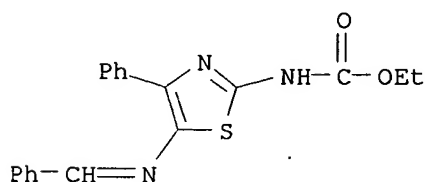
1 drop H<sub>2</sub>SO<sub>4</sub>, warmed 3 min. on the steam bath, give 1 g. of the N<sup>5</sup>-Ac derivative, m. 243°, absorption maximum (EtOH) at 2870 Å. (ε 12,000); BzH gives the N<sup>5</sup>-benzylidene derivative, buff, m. 260° (decomposition), absorption maximum (CHCl<sub>3</sub>) at 3560 Å. (ε 22,000). II (16 g.) and 80 cc. 5% Na<sub>2</sub>CO<sub>3</sub>, heated 10 min. on the steam bath, gives 4 (or 5)-carbethoxyamino-2-mercaptoglyoxaline (III), m. 173°, absorption maximum (EtOH) at 2690 Å. (ε 13,850); NaOH gives a deep blue solution III and Ac<sub>2</sub>O-H<sub>2</sub>SO<sub>4</sub> give 4 (or 5)-carbethoxyamino-2-(acetylmercapto)glyoxaline, m. 169°, absorption maximum (CHCl<sub>3</sub>) at 2560, 3150, 3260 Å. (ε 10,100, 7800, 7800). III (1 g.) and 2 g. Raney Ni in 25 cc. EtOH, refluxed 40 min., give 0.45 g. 4 (or 5)-carbethoxyaminoglyoxaline. MeCH(NH<sub>2</sub>)CN (10 g.) in 50 cc. ether, treated at about 10° with 8 cc. I in 25 cc. ether and the solution kept 6 days, gives 3.7 g. of the 4-Me derivative (IV) of II, yellow, m. 145°, absorption maximum (CHCl<sub>3</sub>) at 2650 Å. (ε 7450). Pure MeCH(NH<sub>2</sub>)CN (11 g.) in 25 cc. ether, treated with 10 cc. I in 25 cc. ether at 0 to -5° and the solution kept overnight, gives 7.3 g. α-(carbethoxythioureido)propionitrile (V), m. 108°, light absorption (CHCl<sub>3</sub>) at 2460 Å. (ε 15,600); V slowly cyclizes to IV; refluxing 1 hr. in EtOH or heating 10 min. at 118° gives a quant. yield of IV. Crude MeCH(NH<sub>2</sub>)CN (1.5 cc.), cautiously treated with 3 cc. I, gives 2-carbethoxyamino-5-(carbethoxythioureido)-4-methylthiazole, cream, m. 233°, absorption maximum (dioxane) at 2600, 3240 Å. (ε 21,600, 7650); it results also on boiling 0.1 g. IV and 3 drops I in 2 cc. C<sub>5</sub>H<sub>5</sub>N. V (0.7 g.) and 10 cc. 10% Na<sub>2</sub>CO<sub>3</sub>, refluxed 10 min., give 0.7 g. 5-carbethoxyamino-2-mercapto-4-methylglyoxaline (VI), m. 244° (decomposition), absorption maximum (EtOH) at 2230, 2670 Å. (ε 6250, 14,300); it was prepared also from IV; 2 g. VI and 4 g. Raney Ni in 40 cc. EtOH, refluxed 1 hr., give 1.1 g. 5-carbethoxyamino-4-methylglyoxaline, m. 167° (decomposition). I (15 g.), slowly added to 15 g. PhCH(NH<sub>2</sub>)CN in 100 cc. ether and the crude product crystallized from EtOH, gives 13 g. α-(carbethoxythioureido)benzyl cyanide (VII), m. 131°, absorption maximum (EtOH) at 2650 Å. (ε 15,250), and, on dilution of the alc. filtrate, 5 g. 5-amino-2-carbethoxyamino-4-phenylthiazole (VIII), buff, m. 167°; VIII results on boiling VII 1.5 hrs. with EtOH. I and VII in ether give 2-carbethoxyamino-5-(carbethoxythioureido)-4-phenylthiazole, buff, m. 194°, absorption maximum at 2650, 3380 Å. (ε 16,550, 5125). VIII and Ac<sub>2</sub>O-H<sub>2</sub>SO<sub>4</sub> give 5-acetamido-2-(carbethoxyimino)-3-acetyl-4-phenyl-4-thiazoline, m. 169°, absorption maximum (EtOH) at 2300, 2700 Å. (ε 48,580, 26,025); BzH in boiling EtOH yields the benzylidene derivative of VIII, bright yellow, m. 166°, absorption maximum at 2600, 3850 Å. (ε 28,450, 19,650) (also prepared from VII). VII (5 g.) and 80 cc. 10% Na<sub>2</sub>CO<sub>3</sub>, heated to boiling, gives 5-carbethoxyamino-2-mercapto-4-phenylglyoxaline, m. 228° (decomposition), absorption maximum at 2690, 2960 Å. (ε 15,775, 15,775); refluxed 40 min. with Raney Ni in EtOH, it yields 5-carbethoxyamino-4-phenylglyoxaline, m. 172°, absorption maximum (AcOEt) at 2640 Å. (ε 16,150). BzNCS (27.5 cc.) in 25 cc. ether, added to 26 g. NCCH(NH<sub>2</sub>)CO<sub>2</sub>Et in 200 cc. ether at 0° and the solution kept overnight, gives 52 g. Et 5-amino-2-benzamido-4-thiazolecarboxylate (IX), lemon, m. 190°, absorption maximum (CHCl<sub>3</sub>) at 3030 Å. (ε 13,700); IX (3 g.) and 15 cc. Ac<sub>2</sub>O, refluxed 15 min., give 4.2 g. Et 5-acetamido-2-(benzoylimino)-3-acetyl-4-thiazoline-4-carboxylate, m.

236°, absorption maximum (CHCl<sub>3</sub>) at 3000 Å. (ε 23,250). IX (3 g.) and 1.5 cc. BzNCS in 7 cc. C<sub>5</sub>H<sub>5</sub>N, heated to boiling and the cooled solution diluted with 20 cc. MeOH, give 3.4 g. Et 2-benzamido-5-(benzoylthioureido)-4-thiazolecarboxylate, pale yellow, m. 232° (decomposition), absorption maximum (CHCl<sub>3</sub>) at 2370, 2880, 3630 Å. (ε 27,250, 30,200, 14,050). IX (5 g.) and 200 cc. 2% aqueous K<sub>2</sub>CO<sub>3</sub>, refluxed 45 min., give 3.7 g. IX and 1.2 g. 5-amino-2-benzamido-4-thiazolecarboxylic acid (X), m. 206°; refluxed with EtOH-HCl, it yields the HCl salt of IX, cream, m. 227° (decomposition); with Ac<sub>2</sub>O it gives X. IX (5 g.), refluxed 45 min. with 100 cc. 10% NaOH, gives 2-thiohydantoin and BzOH; thus IX is not isomerized but undergoes extensive changes. NCCH(NH<sub>2</sub>)CO<sub>2</sub>Et (26 g.) in 200 cc. ether at 0°, treated with 26 cc. I in ether and the clear solution kept overnight, gives (carbethoxythioureido)carbethoxyacet onitrile, NCCH(CO<sub>2</sub>Et)NHCSNHCO<sub>2</sub>Et (XI), decompose 190°, absorption maximum (CHCl<sub>3</sub>) at 2720 Å. (ε 8550); 4 g. XI and 80 cc. 5.5% HCl-EtOH on refluxing gives 3.8 g. Et 5-amino-2-carbethoxyamino-4-thiazolecarboxylate-HCl, m. 177° (decomposition); HBr salt, m. 185°. XI (2 g.) and 1 cc. I in 10 cc. C<sub>5</sub>H<sub>5</sub>N, heated to boiling, give 2.3 g. Et 2-carbethoxyamino-5-(carbethoxythioureido)-4-thiazolecarboxylate, pale-lemon, m. 209° (decomposition), absorption maximum (CHCl<sub>3</sub>) at 2640, 3470 (ε 19,100, 14,050). XI (5 g.) and 65 cc. 2 N NaOH at room temperature give the pale yellow Na derivative, absorption maximum (0.5 N NaOH) at 2870 Å. (ε 17,750); with Me<sub>2</sub>SO<sub>4</sub> in 4% NaOH it yields (N-carbethoxy-S-methylisothioureido)carbethoxyacetoneitrile, pale-lemon, m. 131°, absorption maximum (CHCl<sub>3</sub>) at 2780 Å. (ε 12,850). XI (3 g.) and 10 cc. Ac<sub>2</sub>O, refluxed 30 min., give 2.6 g. Et 2-carbethoxyamino-5-acetamido-4-thiazolecarboxylate, m. 122°, absorption maximum (CHCl<sub>3</sub>) at 2630, 3090 Å. (ε 15,050, 15,050); boiling H<sub>2</sub>O gives a compound C<sub>9</sub>H<sub>13</sub>O<sub>4</sub>N<sub>3</sub>S (?), m. 175°, absorption maximum (CHCl<sub>3</sub>) at 2640, 3080 Å. (ε 9800, 9800). XI (2 g.) and 5% MeOH-KOH give the crude K salt, acidification of an aqueous solution of which with AcOH gives 1.6 g. (carbethoxythioureido)carbomethoxyacetoneitrile, m. 164°, absorption maximum (CHCl<sub>3</sub>) at 2690, 2820 Å. (ε 10,780, 10,780); the solution in 2 N NaOH quickly deposits the Na salt. XI is practically unchanged on heating 5 g. with 4 cc. liquid NH<sub>3</sub> in 25 cc. EtOH at 120°. C<sub>5</sub>H<sub>5</sub>N.HSCN (1 g.) and 0.3 g. H<sub>2</sub>NCH<sub>2</sub>CN in AcOEt give 0.5 g. aminoacetoneitrile [(cyanomethyl)ammonium]thiocyanate, NCCH<sub>2</sub>NH<sub>2</sub>.HNCS, m. 123°; this results also from H<sub>2</sub>NCH<sub>2</sub>CN and HCNS in ether; it is unstable in air, and with NaOH and BzCl yields hippuronitrile; the thiocyanate of PhCH(NH<sub>2</sub>)CN m. 141.5° and that of NCCH(NH<sub>2</sub>)CO<sub>2</sub>Et m. 113-14°. The possibility of effecting the complete series of changes with any one nitrile depends markedly on the nature of the compound employed and perhaps more on the electroneg. character of the group attached to the aminonitrile C atom.

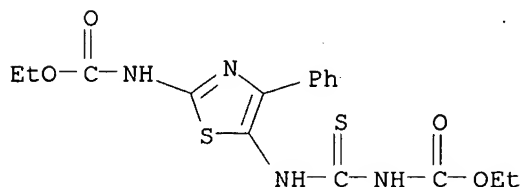
IT 858486-27-8P, 2-Thiazolecarbamic acid, 5-benzylideneamino-4-phenyl-, ethyl ester 859481-03-1P, 2-Thiazolecarbamic acid, 5-(3-carboxy-2-thioureido)-4-phenyl-, diethyl ester 859481-35-9P, 2-Thiazolecarbamic acid, 5-amino-4-phenyl-, ethyl ester  
 RL: PREP (Preparation)  
 (preparation of)

RN 858486-27-8 CAPLUS

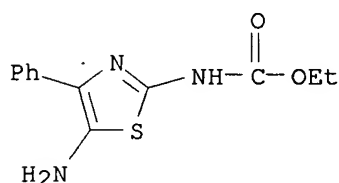
CN 2-Thiazolecarbamic acid, 5-benzylideneamino-4-phenyl-, ethyl ester (5CI)  
 (CA INDEX NAME)



RN 859481-03-1 CAPLUS  
 CN 2-Thiazolecarbamic acid, 5-(3-carboxy-2-thioureido)-4-phenyl-, diethyl ester (5CI) (CA INDEX NAME)



RN 859481-35-9 CAPLUS  
 CN 2-Thiazolecarbamic acid, 5-amino-4-phenyl-, ethyl ester (5CI) (CA INDEX NAME)



L16 ANSWER 15 OF 15 CAPLUS COPYRIGHT 2007 ACS on STN

AN 1949:6451 CAPLUS

DN 43:6451

OREF 43:1400e-i,1401a-h

TI Azole series. VI. Interaction of  $\alpha$ -amino nitriles and isothiocyanates

AU Cook, A. H.; Downer, J. D.; Heilbron, Ian

SO Journal of the Chemical Society (1948) 1262-7

CODEN: JCSOA9; ISSN: 0368-1769

DT Journal

LA Unavailable

OS CASREACT 43:6451

AB BzNCS (12.2 cc.) in 20 cc. ether, added (15 min.) to 5 g. H<sub>2</sub>NCH<sub>2</sub>CN in 70 cc. ether at 0°, gives 13 g. 5-amino-2-benzamidothiazole (I), m. 157° (decomposition), absorption maximum at 2820 and 2400 A. ( $\epsilon$  16,400 and 21,900) (CHCl<sub>3</sub>). H<sub>2</sub>NCH<sub>2</sub>CN (20 g.) in 200 cc. ether at 0°, treated (20 min.) with 58 g. BzNCS in 140 cc. PhMe, gives 81% I; picrate, yellow, m. 163°; HCl salt, m. 200-1° (decomposition). I (1.5 g.) in 20 cc. C<sub>5</sub>H<sub>5</sub>N containing 1 cc. BzNCS, heated to boiling, gives 1.5 g. 2-benzamido-5-(benzoylthioureido)thiazole (II), lustrous green-yellow, m. 229° (decomposition), absorption maximum at 2350, 2810, and 3530 A. ( $\epsilon$  28,300, 29,800, and 12,800) (in dioxane), 2880 A. ( $\epsilon$  9550) (in 0.1 N KOH). II results in 5-g. yield from 17 g. H<sub>2</sub>NCH<sub>2</sub>CN.H<sub>2</sub>SO<sub>4</sub> in 60 cc. C<sub>5</sub>H<sub>5</sub>N and 27 g. BzNCS in 200 cc. PhMe on slowly heating to boiling. II (1 g.) in 8 cc. N NaOH, shaken with Me<sub>2</sub>SO<sub>4</sub>, gives 1 g. of the di-Me derivative, yellow, m. 180° (decomposition), absorption maximum at 2490, 2810, and 3340 A. ( $\epsilon$  25,400, 20,900, and 22,150) (in CHCl<sub>3</sub>). H<sub>2</sub>NCH<sub>2</sub>CONH<sub>2</sub> (10 g.) in 100 cc. EtOH and 12 cc. H<sub>2</sub>O, stirred at about 0° while 18.3 g. BzNCS is added (5 min.), gives N-(benzoylthioureido)acetamide (III), m. 209-10° (slight decomposition), absorption maximum at 2390 and 2810 A. ( $\epsilon$  23,250 and 9950) (in dioxane); it is only weakly basic and does not react further with BzNCS. III (3 g.) and 0.5 cc. PBr<sub>3</sub> in 50 cc. dioxane give 3.8 g. of the HBr salt

of I, cream, m. 198° (decomposition). I (5 g.) and 20 cc. Ac<sub>2</sub>O, refluxed 15 min., give 6.5 g. of a product which, recrystd. from EtOH, gives 5-acetamido-2-(benzoylimino)-3-acetylthiazoline (IV), m. 185°, absorption maximum at 2860 Å. (ε 13,650) (CHCl<sub>3</sub>), 2280, 3360 Å. (ε 14,550 and 14,550) (0.1 N KOH); the mother liquor from IV yields 1.7 g. of a hydrate of 4(5)-benzamido-2-mercapto-1(or 3)-acetyl-glyoxaline (?) (V), m. 249-50°; anhydrous amorphous form m. 251°; absorption maximum at 2290, 3150 Å. (ε 13,050, 12,400) (EtOH), 2250, 3470 Å. (ε 15,150, 12,800) (0.1 N KOH); V results also by boiling 1.5 g. IV with 20 cc. 10% Na<sub>2</sub>CO<sub>3</sub> or with Raney Ni in EtOH. V (0.8 g.) and 6 cc. Ac<sub>2</sub>O, refluxed 10 min., give 4-benzamido-2-(acetylmercapto)-3-acetylimidazole (?), green yellow, m. 199°, absorption maximum at 3150 Å (ε 12,100) (CHCl<sub>3</sub>), 2270, 3470 Å. (ε 17,400, 14,550) (0.1 N KOH); crystallization from C<sub>5</sub>H<sub>5</sub>N gives V. I (3 g.) and 2 cc. BzCl in 50 cc. C<sub>6</sub>H<sub>6</sub>, refluxed 90 min., give 2,5-dibenzamidothiazole, with 1 mol. H<sub>2</sub>O, m. 295° (decomposition); absorption maximum at 2280, 3240 Å. (ε 22,850, 17,050) (EtOH). I (2 g.) and 1 cc. BzH in 40 cc. EtOH, refluxed 30 min., give 2.7 g. of the benzylidene derivative, yellow, m. 233°, absorption maximum at 2350, 3050, and 3660 Å. (ε 23,000, 8000, 31,950) (CHCl<sub>3</sub>). I refluxed 3 h. in EtOH while treated with HCl, gives Et γ-benzoyl-δ-thiohydantoate; refluxed 40 min. with concentrated HCl, I yields the free acid. I (5 g.), refluxed 5 min. with 60 cc. 10% Na<sub>2</sub>CO<sub>3</sub>, gives 4.3 g. 4(or 5)-benzamido-2-mercaptoglyoxaline (VI), decompose 240°, absorption maximum at 2670, 2280, 3050 Å. (ε 17,100, 17,100, 6800) (EtOH); p-NaO<sub>3</sub>SC<sub>6</sub>H<sub>4</sub>N<sub>2</sub>Cl gives a carmine dye; concentrated HCl (boiled 45 min.) gives 2-thiohydantoin. VI (12 g.) in 400 cc. EtOH, refluxed 1 h. with 24 g. Raney Ni, gives 6 g. 4(or 5)-benzamidoglyoxaline, m. 217° (slight decomposition), absorption maximum at 2270 Å. (ε 9350) (CHCl<sub>3</sub>); 1 g. and 10 cc. Ac<sub>2</sub>O, refluxed 30 min., give 0.6 g. 5-benzamido-2-(acetylmercapto)imidazole (?), m. 204°. PhCH(NH<sub>2</sub>)CN (15 g.) and 20 g. BzNCS in 230 cc. PhMe, warmed slightly and kept 3 days, give 22 g. 5-amino-2-benzamido-4-phenylthiazole (VII), yellow, m. 179°, absorption maximum at 3090 Å. (ε 12,100) (CHCl<sub>3</sub>), 2310, 3100 Å. (ε 21,550, 4425) (0.1 N KOH); the diazo solution gives a red dye with 2-ClOH<sub>7</sub>OH. VII and an excess BzNCS in C<sub>5</sub>H<sub>5</sub>N, refluxed 1 min., give 2-benzamido-5-(benzoylthioureido)-4-phenylthiazole, m. 203°; it results in 6.7-g. yield from 5 g. PhCH(NH<sub>2</sub>)CN and 10 cc. BzNCS in 50 cc. ether on standing overnight; the monohydrate m. 205°, absorption maximum at 2440, 2820, 3760 Å. (ε 43,800, 26,200, 9300) (CHCl<sub>3</sub>), 3380 Å. (ε 12,400) (0.1 N KOH). VII (1 g.) and 10 cc. Ac<sub>2</sub>O, refluxed 2 h., give 0.7 g. 5-acetamido-2-(benzoylimino)-3-acetyl-4-phenylthiazoline, m. 180°, absorption maximum (CHCl<sub>3</sub>) at 2390, 2810, 2040 Å. (ε 35,250, 17,450, 13,300). VII (1.5 g.) and 0.5 cc. BzH in 30 cc. EtOH, refluxed 30 min., give 1.8 g. of the benzylidene derivative, yellow, m. 197-8°, absorption maximum (CHCl<sub>3</sub>) at 2420, 2590, 3070, 3950 Å. (ε 31,000, 31,000, 14,550, 25,650). PhCH(NH<sub>2</sub>)CN (5 g.) and 5.2 cc. PhNCS in 100 cc. ether give 7 g. α-(phenylureido)benzyl cyanide (VIII), m. 155°. Ureidoacetonitrile, α-ureidobenzyl cyanide, and VIII show no tendency to pass into aminooxazoles. PhCH(NH<sub>2</sub>)CN (8 g.) and 7 cc. PhNCS, heated to boiling, give 3 g. 5-amino-2-anilino-4-phenylthiazole (IX), m. 190°, absorption maximum at 3130 Å. (ε 15,100) (EtOH), 2290, 3080 Å. (ε 18,700, 6250) (0.1 N KOH); 1 g. IX and 10 cc. Ac<sub>2</sub>O, refluxed 1 h., give 5-acetamido-2-phenylimino-3-acetyl-4-phenylthiazoline, m. 245°, absorption maximum at 2950 Å. (ε 18,250) (CHCl<sub>3</sub>), 2950 Å. (ε 18,250) (0.1 N KOH). H<sub>2</sub>NCH<sub>2</sub>CN (10 g.) and 20 cc. PhNCS in 25 cc. ether give 31.5 g. of presumably 5-amino-2-anilinothiazole, which could not be crystallized; 2.3 g. and 2 cc. PhNCS in 5 cc. C<sub>5</sub>H<sub>5</sub>N, boiled 1 min., give 2 g. 2-anilino-5-(phenylthioureido)thiazole, yellow, m. 221°, absorption maximum (CHCl<sub>3</sub>) at 3020, 3870 Å. (ε 12,050, 28,700). These results indicate that α-thioureido nitriles (e. g., NCCH<sub>2</sub>NHCSNHBz) enjoy at

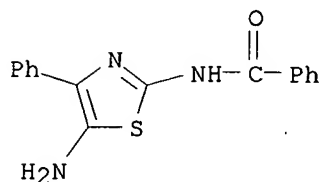
most a transitory existence, whereas corresponding ureas show no tendency to undergo cyclization.

IT 850852-75-4P, Thiazole, 5-amino-2-benzamido-4-phenyl-  
859325-89-6P, Urea, 1-(2-benzamido-4-phenyl-5-thiazolyl)-3-benzoyl-  
2-thio- 874508-82-4P, Thiazole, 2-benzamido-5-benzylideneamino-4-phenyl-

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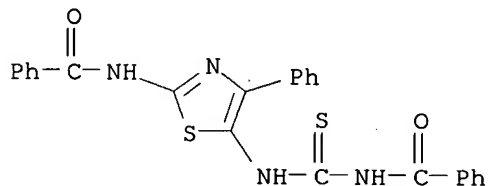
RN 850852-75-4 CAPLUS

CN Benzamide, N-(5-amino-4-phenyl-2-thiazolyl)- (9CI) (CA INDEX NAME)



RN 859325-89-6 CAPLUS

CN Urea, 1-(2-benzamido-4-phenyl-5-thiazolyl)-3-benzoyl-2-thio- (5CI) (CA INDEX NAME)



RN 874508-82-4 CAPLUS

CN Thiazole, 2-benzamido-5-benzylideneamino-4-phenyl- (5CI) (CA INDEX NAME)

